Tautomerism, Ionization, and Bond Dissociations of 5-Nitro-2,4-dihydro-3*H*-1,2,4-triazolone

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Abstract: Tautomerization, ionization, and bond dissociations of the insensitive high-energy explosive 5-nitro-2,4-dihydro-3*H*-1,2,4-triazolone (NTO) were studied by molecular orbital SCF and MP2 theories and with the Becke3LYP hybrid density functional using the 6-31+G* and 6-311+G** basis sets. Energies computed with these methods were compared against accurate G2 energies for the tautomerization, ionization, and bond dissociations of nitromethane. The Becke3LYP and MP2/6-31+G* structures of NTO anion **9** compare well with the reported X-ray structure of the NTO diaminoguanidinium salt. The IR frequencies calculated with Becke3LYP compare well with those observed for crystalline NTO. Two enol tautomers (**2** and **4**) with 1*H*-1,2,4-triazole skeletons are only 4 kcal/mol at MP2/6-311+G** (and 9 kcal/mol at Becke3LYP/6-311+G**) less stable than NTO, while the two *aci*-nitro tautomers (**5** and **6**) are ca. 30 kcal/mol less stable than NTO. Comparisons of bond lengths, calculated proton chemical shifts, and magnetic susceptibility anisotropies show the enol tautomers are more aromatic than NTO, which accounts for their enhanced stabilities. NTO anion **9** is also more aromatic than NTO, which partly explains its small proton affinity of 321 kcal/mol calculated at Becke3LYP/6-311+G**+ZPE. The estimated N−H and C−NO_2 bond dissociation energies for NTO are respectively 93 and 70 kcal/mol, and that for the N−OH bond of the *aci*-nitro tautomer **5** is 38 kcal/mol. Some possible processes in the initial stages of NTO decomposition are bimolecular hydrogen atom transfers (in the condensed phase), C−NO_2 bond homolysis (at high temperatures or under conditions of shock or impact), and homolysis of the N−OH bond in the *aci*-nitro tautomers.

Introduction

5-Nitro-2,4-dihydro-3*H*-1,2,4-triazol-3-one (NTO) is a high energy explosive[1] that is less sensitive than the commonly used nitramine explosives 1,3,5-trinitrohexahydro-*s*-triazine (RDX)[2] and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).[3] Considerable experimental effort has been spent to understand the mechanism for thermal decomposition of NTO, but the mechanism is still unknown.

A key to unraveling the mechanism is identifying and quantifying the gaseous decomposition products. Several groups have recently carried out experiments to determine these products.[4] The results depend both on the analytical method and on whether the sample is heated slowly or rapidly. We highlight a few of these studies.

Williams, Palopoli, and Brill[4b] found that the IR-active gases formed during the first stages of the decomposition of NTO, rapidly heated to 450 °C, were NO, CO_2, N_2O, HCN, HNCO, and small amounts of CO (water was excluded). At low pressures they determined that the formation of NO is dominant whereas CO_2 formation is dominant at high pressures. Botcher, Beardall, and Wight[4e] pyrolyzed a film of NTO with a pulsed infrared laser, and found that the first product formed was CO_2. They also found that no NO_2 was formed and that CO_2 originated from the carbonyl carbon of NTO. Oxley and co-workers[4a] heated samples of NTO in sealed tubes at temperatures ranging from 160 to 280 °C and detected the gaseous products by GC. They concluded that the gas composition was mostly CO_2 and N_2, with small amounts of NO, N_2O, and CO also being formed. Other experiments to determine the gaseous products from NTO decomposition were done by Ostmark, Bergman, and Aqvist[4d] using GC/MS analysis, and by Prabhakaran and co-workers[4c] using IR analysis. All these product analyses suggest that the C−NO_2 bond dissociation does not initiate the controlled thermal decomposition of NTO, in contrast to similar studies that show initial N−NO_2 bond dissociation is an important pathway in the decompositions of RDX and HMX.[2,3]

Several experimental groups have studied the global kinetics for the controlled decomposition of NTO at temperatures below 600 K in the condensed phase.[5] The process is more complex than the unimolecular decomposition in the gas phase, because bimolecular reactions, autocatalysis, and physical phenomena such as heat and mass transfer affect the rate in the condensed phase.[6]

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Table 1. Energies (in atomic units; 1 hartree = 627.51 kcal/mol) for NTO Tautomers, Anions, and Radicals

	(U)HF		(U)MP2		B3LYP		
compd	6-31+G*	6-311+G**	6-31+G*	6-311+G**	6-31G*	6-311G**	ZPE[a]
1	−519.152 77	−519.282 92	−520.625 80	−520.850 36	−522.000 51	−522.136 87	45.99
2	−519.142 20	−519.274 69	−520.615 57	−520.843 70	−521.985 51	−522.123 24	46.16
3	−519.130 76	−519.262 57	−520.604 53	−520.831 59	−521.976 41	−522.113 58	45.78
4	−519.135 72	−519.267 85	−520.615 15	−520.843 01	−521.984 12	−522.121 52	46.13
5	−519.101 75	−519.233 88	−520.570 92	−520.797 56	−521.955 97	−522.093 13	44.56
6	−519.087 49	−519.222 30	−520.573 12	−520.804 72	−521.949 44	−522.088 55	45.28
7	−519.126 00	−519.256 89	−520.595 82	−520.822 44	−521.971 43	−522.108 09	46.25
8	−518.613 77	−518.737 95	−520.106 12	−520.319 08	−521.479 74	−521.611 17	36.38
9	−518.624 18	−518.750 16	−520.112 97	−520.328 15	−521.480 51	−521.613 17	37.02
10	−518.526 53	−518.652 48	−519.960 38	−520.176 62	−521.335 47	−521.466 56	35.68
11	−518.532 08	−518.658 18	−519.965 35		−521.342 00	−521.473 83	36.01
12	−315.038 00	−315.115 60	−315.927 90		−316.809 49	−316.891 64	34.66
13	−443.726 08	−443.831 21			−446.148 00	−446.258 79	31.10
14	−315.025 07	−315.104 87			−316.791 54	−316.874 73	35.11
15	−443.612 77	−443.717 52			−446.058 99	−446.168 71	34.19
NO_2	−204.038 32	−204.092 49	−204.578 56	−204.671 29	−205.083 88	−205.140 47	6.15
OH	−75.386 74	−75.414 65	−75.531 33	−75.581 26	−75.533 50	−75.762 29	5.70

[a] Zero-point vibrational RHF/6-31+G* energy in kcal/mol.

The temperature dependence of the rate constant for the global process is described by the Arrhenius equation, $k = A \exp(-E_a/RT)$. Williams and Brill have noticed that the Arrhenius parameters for NTO reported by different groups vary greatly.[5] However, an approximately linear relation is found between ln A and E_a, so that different (E_a − ln A) pairs give similar rate constants over the limited temperature range over which the experiments were conducted.[6] Several groups attempting to observe the thermal decomposition of NTO were in reality observing the sublimation of NTO, or a combination of sublimation and decomposition. The decomposition reaction has Arrhenius parameters $E_a = 78-87$ kcal/mol and ln $A(s^{-1}) = 67-78$, while the parameters for the sublimation process are much smaller.

Brill[5] has warned that the Arrhenius parameters for the global decomposition process cannot be interpreted in the same way as for elementary reactions. In particular, it is not possible to relate the E_a value directly to bond strengths of the molecule. However, decomposition rates during the induction phase are more likely to relate to uni- or bimolecular reactions of the parent explosive molecule than are rates during the latter stages of the decomposition.

This ab initio molecular orbital study aims to contribute to the challenge of unraveling the chemical pathways for NTO decomposition by determining energetics for tautomerism, ionization, and bond dissociations of NTO. This approach is related to our work on the nitroaromatics picric acid, picramide, and trinitrotoluene (TNT),[7] and extends a previous *ab initio* study of NTO tautomerism by Ritchie[8] at the RHF/6-31G*//RHF/3-21G level[9] of theory.

Computational Methods

All *ab initio* molecular orbital calculations[9] were carried out using the Gaussian 94 suite of programs.[10,11] The optimized geometries and harmonic vibrational frequencies for 21 neutral structures, 4 anions, and 6 radicals of NTO were computed at the (U)HF/6-31+G* level of theory using IBM RS/6000 (3BT) workstations. The split valence 6-31+G* basis set[12] includes diffuse functions, denoted by +,[13] and heavy atom d-polarization functions, denoted by an asterisk, for a total of 175 basis functions for the NTO molecule. Diffuse functions are desired for proper description of the nitrogen lone pairs of the anions, and they were included in all calculations for consistency.

All structures but one were constrained to have planar C_s symmetry. This initial screening showed most of these planar geometries are energy minima with no imaginary vibrational frequencies. Two neutral structures and one anion are transition structures having a single imaginary frequency, and two other neutral structures each have two imaginary frequencies.

After calculating the complete set of structures at the SCF level, the geometries for nine of the more pertinent neutral and anion structures were optimized at MP2(fc)/6-31+G*, which uses second-order Møller−Plesset perturbation theory[14] in the frozen core approximation to account for electron correlation. Single-point energies[9] for the nine structures were then evaluated at MP2(fc)/6-311+G** using a Cray C90. The essentially triply split 6-311+G** basis set[15] includes polarization functions on all atoms, and has a total of 210 basis functions for NTO.

Finally, the geometries of the same nine structures and six radicals were optimized using the Becke3LYP (B3LYP) hybrid density functional[16] and the 6-31+G* basis set. Single-point energies for these 15 structures were then computed at the B3LYP/6-311+G** level. The density functional method was compared with the MP2 and RHF methods with regard to accuracy and demand on computer resources.

Energies for the seven tautomers, two anions, and six radicals of NTO are given in Table 1. The structures are shown in Figure 1, and a summary of bond lengths is given in Table 2. The structures in Figure 1 can be varied by changing the conformations of the enol (−OH) and *aci*-nitro ($-NO_2H$) groups. These changes lead to a large number of higher energy structures which are omitted for the sake of clarity.

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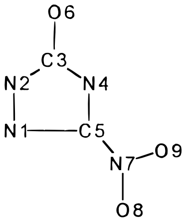
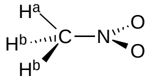
Table 2. B3LYP/6-31+G* Optimized Bond Lengths (in Å)



compd	N1N2	N2C3	C3N4	N4C5	C5N1	C3O6	C5N7	N7O8	N7O9	av CN[a]
1	1.358	1.399	1.402	1.368	1.297	1.213	1.445	1.223	1.237	1.366 ± 0.049
2	1.359	1.355	1.316	1.358	1.318	1.334	1.464	1.228	1.227	1.337 ± 0.023
3	1.373	1.321	1.355	1.374	1.306	1.332	1.439	1.222	1.241	1.339 ± 0.031
4	1.351	1.335	1.357	1.319	1.343	1.337	1.448	1.238	1.222	1.338 ± 0.016
5	1.275	1.463	1.399	1.364	1.388	1.206	1.319	1.392	1.248	1.403 ± 0.042
6	1.307	1.396	1.315	1.366	1.367	1.328	1.357	1.209	1.382	1.361 ± 0.034
7	1.405	1.426	1.425	1.282	1.365	1.207	1.480	1.234	1.216	1.374 ± 0.068
8	1.333	1.404	1.398	1.374	1.332	1.237	1.390	1.248	1.266	1.377 ± 0.033
9	1.359	1.416	1.373	1.344	1.328	1.243	1.453	1.241	1.236	1.365 ± 0.039
10	1.310	1.426	1.419	1.335	1.350	1.214	1.447	1.223	1.237	
11	1.313	1.431	1.397	1.303	1.373	1.217	1.476	1.227	1.223	
12	1.402	1.375	1.420	1.364	1.267	1.218				
13	1.265	1.470	1.396	1.374	1.409	1.204	1.291	1.230		
14	1.391	1.348	1.326	1.348	1.301	1.338				
15	1.350	1.358	1.324	1.363	1.324		1.464	1.228	1.225	

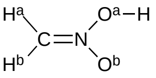
[a] Average C−N bond lengths of the ring carbon−nitrogen bond lengths of the NTO tautomers. Errors are standard deviations in the average bond lengths.

Table 3. Geometrical Parameters for Nitromethane and *aci*-Nitromethane



(a) Nitromethane

bonds, angles	HF	MP2	B3LYP	exp[b]
$\mathrm{C{-}H_b}$	1.076	1.088	1.089	1.088(1)
$\mathrm{C{-}H_a}$	1.080	1.091	1.093	
C−N	1.481	1.491	1.500	1.489(5)
N−O	1.192	1.244	1.228	1.224(5)
$\mathrm{H_a{-}C{-}N}$	106.4	107.0	106.6	107.2
$\mathrm{H_b{-}C{-}N}$	107.9	107.7	108.1	
$\mathrm{H_b{-}C{-}H_b}$	113.0	112.8	112.9	
C−N−O	117.2	117.3	117.2	
O−N−O	125.6	125.4	125.5	125.3



(b) *aci*-Nitromethane[c]

bonds, angles	HF	B3LYP	MP2
$\mathrm{C{-}H_a}$	1.068	1.082	1.078
$\mathrm{C{-}H_b}$	1.068	1.083	1.078
C=N	1.265	1.300	1.314
$\mathrm{N{-}O_a}$	1.352	1.419	1.430
$\mathrm{N{-}O_b}$	1.245	1.242	1.243
O−H	0.955	0.973	0.984
$\mathrm{H_a{-}C{-}N}$	118.8	118.3	117.9
H−C−H	124.2	124.9	125.9
$\mathrm{C{-}N{-}O_a}$	116.1	114.1	113.0
$\mathrm{C{-}N{-}O_b}$	129.1	130.5	131.2
N−O−H	103.0	101.0	100.4

[a] Using the 6-31+G* basis set. Bond lengths in Å and angles in deg. [b] Reference 44. [c] Using the 6-31+G* basis set.

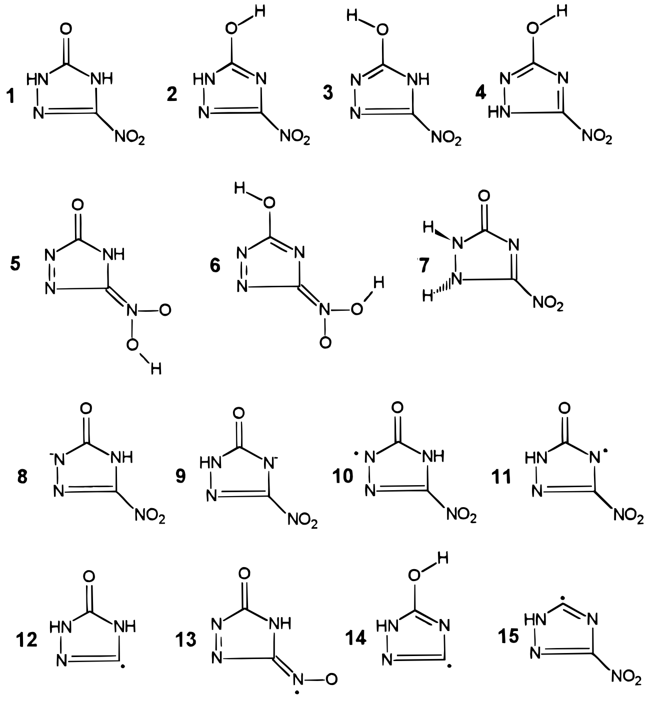


Figure 1. Tautomers, radicals, and anions of NTO.

Calculations were also done on tautomerization, ionization, and bond dissociations for nitromethane, as a small test molecule. Again, these calculations were done at the SCF, MP2, and B3LYP theoretical levels, with the 6-31+G* basis for geometry optimizations and frequencies, and the larger 6-311+G** and 6-311+G(2d,2p) basis for improved single-point energies. The geometries for nitromethane and *aci*-nitromethane are presented in Tables 3a and 3b, and the energies are given in Table 4. These are compared with more accurate energies computed using G1 and G2 theories.[17,18]

The N−OH bond dissociation energy in *aci*-nitromethane was computed using Pople's quadratic configuration interaction method

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Table 4. Energies for Nitromethane Tautomerism, Ionization, and C−N and C−H Bond Homolyses[a]

	$CH_3NO_2 \rightarrow CH_2NO_2H$			$CH_3NO_2 \rightarrow CH_2NO_2^- + H$			$CH_3NO_2 \rightarrow CH_3 + NO_2$			$CH_3NO_2 \rightarrow CH_2NO_2 + H$		
basis set	HF	MP2	B3L	HF	MP2	B3L	HF	MP2	B3L	HF	MP2	B3L
6-31+G*	19.2	20.6	16.5	359.4	354.1	351.8	37.4	55.6	54.0	73.9	92.4	97.4
6-311+G**	16.2	18.2	13.7	360.7	359.3	352.1	36.1	52.6	52.4	75.7	95.1	98.6
6-311+G(2d,2p)	16.1	15.8	12.7	362.2	356.1	352.6	36.5	54.4	52.9	75.2	95.7	98.4
		G1: 14.1[b]			G1: 355.2,[b] exp. 356.1[d]			G2: 61.0,[c] exp. 59.4[e]			G2: 101.3[c]	

[a] Energies in kcal/mol. Geometries optimized with the 6-31+G* basis set. B3LYP is abbreviated as B3L. All energies are corrected for ZPVE differences using 0.89 scaled RHF/6-31+G* frequencies. [b] Reference 18. [c] This work. [d] Reference 24. [e] Reference 25.

(QCISD(T)),[19,20] which is standard in Gaussian 94, using the 6-311+G** basis. For computing this bond strength, the geometry and harmonic frequencies for the $^2A'$ ground state of the CH_2NO radical were computed using complete active space SCF (CASSCF) theory,[19,20] with an active space of seven electrons in seven molecular orbitals.[20c]

Magnetic properties for the NTO tautomers and anions were computed using the continuous set of guage transformations (CSGT) method,[21] which is standard in Gaussian 94, at the B3LYP/6-311+G** level of theory. Isotropic magnetic shieldings for the hydrogen nuclei were converted to conventional ^1H NMR chemical shifts (δ), referenced to tetramethylsilane (TMS). The computed shielding for the benzene protons was assigned the experimentally observed value for benzene solvent of $\delta = 7.26$ ppm relative to TMS, and the proton shifts for the other structures were then computed using benzene as a secondary reference. The data are presented in Figure 2.

Results and Discussion

Nitromethane. We carried out some preliminary tests on a small molecule, nitromethane. Our purpose here was to compare the SCF, MP2, and B3LYP theories with the highly accurate G1 and G2 theories,[17] for computing bond dissociation, ionization, and tautomerization energies for this small test molecule.

The computed geometries for nitromethane and *aci*-nitromethane and the experimental nitromethane geometry are shown in Table 3, parts a and b. As expected, the N−O bonds are too short at the SCF level. The MP2/6-31+G* geometry of nitromethane agrees better with the experimental geometry, except that the N−O bonds are too long.[18] The N−O bond lengths are better with B3LYP/6-31+G* theory, but otherwise the B3LYP and MP2 geometries are similar.

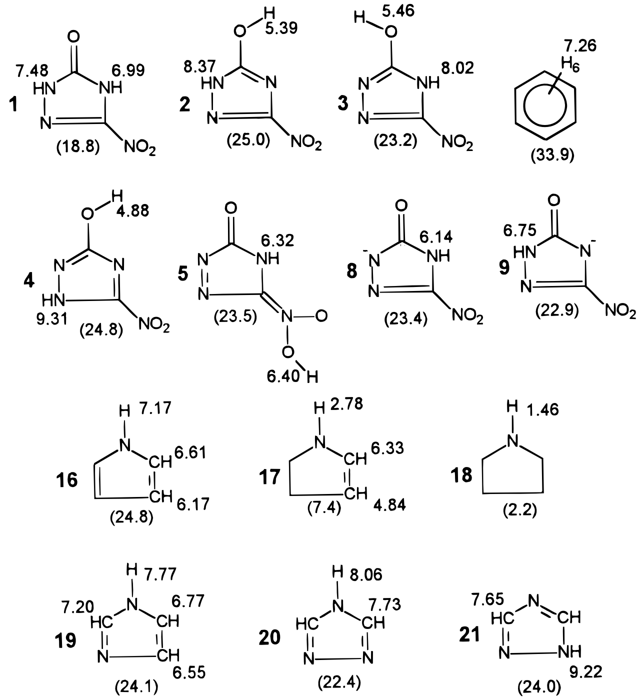

Figure 2. Magnetic susceptibility anisotropies (cgs ppm) and computed ^1H NMR chemical shifts (in parts per million relative to tetramethylsilane) for NTO tautomers and anions, and some related nitrogen heterocycles.

The computed energies for tautomerization, ionization, and C−N and C−H bond homolyses for CH_3NO_2 are summarized in Table 4. These energies are corrected for zero-point vibrational energy (ZPE) differences[22] using scaled (U)HF/6-31+G* frequencies.[9,23] The MP2 and B3LYP energies are quite similar and are better than the Hartree−Fock energies. The experimental gas phase acidity[24] and C−N bond dissociation enthalpy[25] (at 298.15 K) compare very well with the G1 and G2 energies. Comparison of results using the 6-311+G** and 6-311+G(2d,2p) basis sets shows that the MP2 energies are more sensitive to the size of the basis set[26] than those computed with B3LYP. The B3LYP/6-311+G** method underestimates the energy difference for the nitromethane tautomerization and the ionization energy. Both the MP2 and B3LYP methods underestimate the C−N bond dissociation energy by 7−8 kcal/

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(19) The QCISD(T) theory was used in place of G2 theory[17] for computing the N−OH bond dissociation energy. This is because G2 theory relies on geometries computed at the MP2/6-31G* level, and the MP2 geometry for CH_2NO radical is very poor. As a result, the G2 energy for the CH_2NO is too large, and the bond dissociation energy is overestimated by about 20 kcal/mol. The CASSCF geometry for CH_2NO has values of 1.265 and 1.223 Å for the CN and NO bond lengths, and 136.1° for the CNO bond angle, compared with the UMP2/6-31G* values of 1.288 Å, 1.318 Å, and 110.3° for these parameters. For QCISD(T) theory see: Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. Pople, J. A.; Gordon, M. H.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

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mol, but are in fair agreement with the G2 energy for the C−H bond homolysis.

The bond strength for the N−OH bond in *aci*-nitromethane was computed because of the importance of N−OH bond dissociation in the decomposition of nitroaromatic explosives.[27] Dissociation of the N−OH bond of *aci*-nitromethane has been observed,[28] but the dissociation energy is not known. Our computed dissociation energy at QCISD(T)/6-311+G** is 46.4 kcal/mol at 0 K,[19] after correction for zero-point vibrational energies. The B3LYP/6-311+G** bond strength of 48.2 kcal/mol is similar to the QCISD(T) value.

From the results for nitromethane, we expect that reasonable energies and geometries for the NTO tautomers, anions, and radicals can be computed using either MP2 theory or the B3LYP density functional theory with a reasonably good basis set. We next turn to NTO.

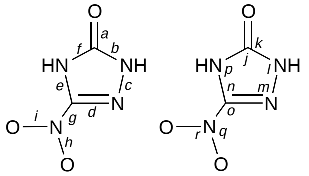
Tautomers and Anions of NTO. (a) NTO Geometry and Vibrational Frequencies. A full comparison of the RHF, MP2, and B3LYP geometries for the NTO global minimum is given in Table 5a. The same information for the NTO anion **9**, along with the X-ray structure of the NTO 1,3-diaminoguanidinium salt, is given in Table 5b. Scaled RHF and B3LYP/6-31+G* vibrational harmonic frequencies for NTO are given in Table 6. These molecules were too large for MP2 frequency calculations. However, it is worth mentioning that Stephens et al.[16] found that the B3LYP/6-31G* vibrational spectrum for 4-methyl-2−oxetanone was superior to the MP2/6-31G* spectrum, at least for the middle range frequencies, 800−1600 cm^{-1}.

It is clear from Table 5a that the MP2 and B3LYP/6-31+G* optimized geometries for NTO differ considerably from those obtained at the SCF level. The differences are within the triazole ring, the nitro group, and the keto bond. The reported HF/3-21G geometry[8] is of similar poor quality to that obtained with the larger 6-31+G* basis set. Studies of the parent nitro ⇌ *aci*-nitro,[18] imine ⇌ enamine,[29] and keto ⇌ enol[30] tautomeric systems showed that the SCF geometries are unsatisfactory, but also showed that MP2 overestimates multiple bond lengths in these systems. Not surprisingly, B3LYP performs better than MP2 in computing multiple bond lengths for the NTO tautomers. This is evident for the nitro group and the keto and enamine bonds. This confirms our conclusions based on nitromethane that B3LYP is a sound method for our purposes.

We compare the SCF (scaled) and B3LYP harmonic vibrational frequencies with the observed[4e] frequencies for NTO. (We would like to compare our geometries with an X-ray crystal structure, but the experimental structure has not been done.) The normal mode frequencies and their assignments are summarized in Table 6. The agreement between the theoretical and experimental frequencies is generally good, but the unscaled B3LYP frequencies for the N−H and C═O stretches are too high by 456 and 128 cm^{-1}, respectively. The corresponding scaled SCF frequencies are also too high, but only by 269 and 61 cm^{-1}. The presence of N−H·····O═C and N−H·····O═N-(O) hydrogen bonding in the solid state might partly explain the disagreement between theory and experiment.

(b) Anion Geometries and Energies. Deprotonation of NTO can occur at N2 or N4 to give anion **8** or **9**. The B3LYP/6-31+G* bond lengths for both anions are given in Table 2. X-ray crystal structures for both the 1,3-diaminoguanidinium and ethylenediammonium salts of NTO have been reported.[31] In both salts NTO is deprotonated at N4, corresponding to our structure **9**. Table 5b presents a comparison of the theoretical geometry for **9** with the experimental geometry of the diaminoguanidinium salt. The geometries illustrate again a satisfactory performance of both the B3LYP and MP2 methods, although the agreement with experiment is not as good as for nitromethane. In particular, the computed C(O)−NH bond is 0.05 Å longer than the experimental bond. Furthermore, the angles around the carbonyl group also differ from the experimental structure. We suggest crystal packing forces may contribute to the differences.

Table 5. Bond Lengths (Å) and Angles (deg) for NTO Anion **7**



(a) Selected Bond Lengths and Bond Angles[a]

	HF	MP2	B3LYP
a	1.192	1.224	1.213
b	1.369	1.392	1.399
c	1.352	1.365	1.358
d	1.258	1.313	1.297
e	1.360	1.360	1.366
f	1.379	1.404	1.402
g	1.443	1.442	1.445
h	1.183	1.240	1.223
i	1.197	1.250	1.237
j	101.7	100.6	100.8
k	129.2	129.8	129.4
l	113.7	115.3	114.6
m	103.7	102.2	103.3
n	113.9	113.8	113.6
o	121.6	122.0	122.0
p	107.0	108.1	107.8
q	114.7	114.9	114.8
r	127.2	127.0	126.7

(b) Theoretical and Experimental Bond Lengths and Bond Angles[b]

	HF	MP2	B3LYP	Expt.[c]
a	1.224	1.253	1.243	1.267(2)
b	1.378	1.409	1.416	1.367(2)
c	1.356	1.362	1.359	1.363(2)
d	1.284	1.346	1.328	1.309(2)
e	1.325	1.345	1.344	1.334(2)
f	1.355	1.379	1.373	1.353(2)
g	1.462	1.445	1.453	1.449(2)
h	1.198	1.252	1.241	1.222(2)
i	1.192	1.251	1.236	1.224(2)
j	105.6	105.1	105.0	107.7(2)
k	123.8	123.8	123.6	125.3(2)
l	112.3	113.9	113.0	111.2(2)
m	99.7	98.7	99.6	100.3(1)
n	119.6	119.1	118.9	118.6(2)
o	118.8	118.6	118.6	120.4(2)
p	102.8	103.2	103.5	102.2(1)
q	118.1	118.4	118.6	118.7(2)
r	124.3	123.8	123.6	124.0(2)

[a] Using the 6-31+G* basis set. [b] Using the 6-31+G* basis set. Same labeling as in Table 5. [c] Reference 31.

The lengthened C═O and C═N bonds and the shortened $^{-}$N−C(O) bond suggest the anions are stabilized by aromatic resonance (see discussion below and Table 2). Interestingly, planar **9** is not a minimum energy structure at the HF/6-31+G*

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Table 6. Theoretical (6-31+G*) and Experimental Vibrational Frequencies (cm^{-1}) for NTO[a]

HF (scaled)	B3LYP	expt[b]	assignment
69 (0.1)	83 (0.2)		a″ NO_2 torsion
142 (1)	144 (2)		a″ skeletal def
199 (6)	201 (5)		a″ NO_2 rock
288 (28)	297 (10)		a″ skeletal def
399 (0.3)	405 (0.4)		a″
438 (5)	460 (3)		a′
453 (9)	476 (3)		a″
504 (273)	534 (226)		a″
567 (9)	578 (6)	610 m	a′
627 (20)	648 (15)	690	a″ ring torsion
734 (32)	727 (4)	740	a″
743 (32)	750 (23)	760 m	a′ ring def
770 (1)	750 (3)	790	a″
833 (61)	830 (39)	830	a′ NO_2 def + ring def
971 (24)	995 (22)		a′ ring def
986 (16)	1011 (14)	1010	a′ ring def
1096 (35)	1105 (60)	1020 m	a′ ring def
1194 (3)	1218 (4)	1190	a′
1271 (53)	1278 (59)	1200 w	a′ ring def
1380 (5)	1377 (354)	1360 s	a′ N−H wag + NO_2 sym str
1410 (155)	1404 (7)		a′
1486 (237)	1477 (68)	1470 (m)	a′ N−H wag + ring def
1648 (587)	1609 (280)	1550 s	a′ C=N str + NO_2 assym str
1681 (82)	1639 (69)	1700 m	a′ C=N str + NO_2 assym str
1781 (1045)	1848 (843)	1720 s	a′ C=O str
3468 (154)	3656 (130)	3200 s	a′ N−H str
3487 (188)	3656 (134)		a′ N−H str

[a] Intensities (kM/mol) are given in parentheses. Assignments are based on the B3LYP/6-31+G* normal modes. [b] Reference 4c.

level, since it possesses a small imaginary frequency of 29 cm^{-1} corresponding to rotation of the NO_2 group. However, at the B3LYP/6-31+G* level all frequencies for planar **9** are real, which characterizes the C_s structure as a minimum. The barrier for rotation around the C−NO_2 bond of **9** appears to be small, which shows that resonance with the nitro group is limited. The C−NO_2 rotation barriers in other conjugated systems are also small. For example, the observed (calculated) barriers are 2.9 (4.6) kcal/mol for nitrobenzene and 5.1 (4.8) kcal/mol for nitroethylene.[32,33]

Structure **9** is the more stable anion, but the energy difference is only 5.7 and 1.3 kcal/mol at MP2 and B3LYP/6-311+G**, respectively. The allylic anion in **9** is delocalized over two nitrogens (N1 and N4), while the negative charge in **8** is delocalized over N2 and C5; one expects **9** to be more stable because nitrogen is more electronegative than carbon. Nevertheless, the difference in energy between **8** and **9** would be even larger in the absence of the electronegative nitro substituent at C5.

NTO is rather acidic. Its aqueous pK_a of 3.67[1] compares with the pK_a values of 4.67[34a] for acetic acid and 2.86[34a] for 2-chloroacetic acid. The gas-phase acidity of NTO is estimated at 321 kcal/mol at both MP2 and B3LYP/6-311+G** after correction for zero-point vibrational energies (see Table 7). NTO is much more acidic in the gas phase than phenol (ΔH_i^{298} = 351.4 kcal/mol)[34b] or formamide (ΔH_i^{298} = 355.0 kcal/mol).[34c] Its acidity compares with that of *p*-nitrophenol (ΔH_i^{298} = 325.6 kcal/mol).[34b] The high acidity of NTO is expected from the delocalized aromatic character of its anions.

Table 7. NTO Deprotonation Energies in kcal/mol[a]

	6-31+G*			6-311+G**		
anions[b]	HF	MP2	B3LYP	HF	MP2	B3LYP
8 (2-N)	329.6	317.5	318.2	333.4	324.8	321.3
9 (4-N)	323.7	313.8	318.3	326.3	319.7	320.6

[a] Energies are corrected for zero-point vibrational energy using RHF/6-31+G* frequencies scaled by 0.89. [b] The NTO anions are also identified by their deprotonation site.

(c) Aromaticity of NTO Tautomers and Anions. NTO and its tautomeric triazoles have aromatic character, which is indicated by their planar geometries. Structure **7** (Figure 1) is the only exception. It has a nonplanar geometry with its adjacent sp^3-hybridized nitrogens pyramidalized in opposite directions, and twisting of its five-membered ring.[35]

We used bond lengths and magnetic properties as criteria to evaluate the aromaticity of the NTO tautomers and anions.[36] In addition, the relative energies of the NTO tautomers and the protonation energies for the NTO anions can be related to differences in aromaticity.

In relating bond lengths to the relative amounts of aromatic character of the NTO tautomers and anions, we note that for an aromatic structure, the ring CN bonds should have nearly the same length, intermediate between that for a typical CN double bond (1.280 Å) and a typical CN single bond (1.385 Å for a $C(sp^2)$ to $N(sp^3)$ bond).[37] Thus, the standard deviation in the CN bond lengths for an aromatic structure should be small.

The standard deviations in the CN bond lengths given in the last column of Table 2 suggest the order of aromaticities for the NTO tautomers and anions is **4** > **2** > **3** > **6** = **8** > **9** > **5** > **1** > **7**. This implies the keto tautomers **1**, **5**, and **7** are less aromatic than the enol tautomers **2**, **3**, and **4**, and also that the keto tautomers are less aromatic than the anions **8** and **9**. One expects, then, that the enol tautomers should be aromatically stabilized relative to NTO (**1**), and the deprotonation of NTO should be made favorable by enhancement of aromaticity. Furthermore, it appears that *aci*-nitro tautomer **6** is more aromatic than *aci*-nitro tautomer **5**. The very long N2C3 bond in **5** accounts for its larger standard deviation. The lengths for the exocyclic C5 to N7 double bonds in **5** and **6** are respectively 1.319 and 1.357 Å, which further suggests that the π-system is more delocalized in the fulvene-like structure **6**.

Magnetic properties such as the magnetic susceptibility anisotropy and magnetic shielding are well established criteria for aromaticity,[36] and these can be computed using *ab initio* MO theory.[37] Aromatic molecules show a characteristic low-frequency shift for the resonance of a hydrogen nucleus bonded to the ring and exalted magnetic susceptibility anistropies.[37] Both of these properties are useful in evaluating aromaticities of the NTO tautomers.

The ^1H NMR chemical shifts (δ) and magnetic susceptibility anisotropies (χ_{anis}) are displayed in Figure 2 for the NTO tautomers and anions, and for several unsubstituted nitrogen-containing heterocycles. We focus on the chemical shifts of the N−H protons (δ_{NH}) for our purpose of ranking aromaticity of the NTO tautomers.

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(35) The pyramidalization angles for nitrogens N1 and N2 in the B3LYP/6-31+G* geometry for structure **7** are respectively 41.8° and 40.3° (these are angles for the NH bond with respect to the CNN plane), which is somewhat smaller than the B3LYP/6-31+G* computed pyramidalization of 67.0° for the nitrogens of hydrazine in its anti conformation. The twisted ring in **7** has a C5−N1−N2−C3 torsion angle of 12.5°.

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Table 8. Relative Energies of NTO Tautomers in kcal/mol[a]

	6-31+G*			6-311+G**		
structures[b]	HF	MP2	B3LYP	HF	MP2	B3LYP
1, NTO	0.0	0.0	0.0	0.0	0.0	0.0
2, (2-H, 3-OH)	6.8	6.6	9.6	5.4	4.4	8.8
3, (4-H, 3-OH)	13.6	13.1	14.9	12.6	11.6	14.4
4, (1-H, 3-OH)	10.8	6.8	10.4	9.6	4.7	9.7
5, (4-H, 5-NO_2H)	30.8	33.2	26.8	29.6	31.9	26.2
6, (3-OH, 5-NO_2H)	40.4	32.5	31.4	37.4	28.0	29.7
7, (1-H, 2-H)	17.0	19.0	18.5	16.5	17.7	18.3

[a] All energies corrected for zero-point vibrational energies using RHF/6-31+G* frequencies, scaled by 0.89. [b] The NTO tautomers are also identified by their characteristic functional groups.

Table 9. Selected Bond Dissociation Energies (in kcal/mol) of NTO, **2** and **5**[a]

	6-31+G*			6-311+G**	
structures	UHF	UMP2	B3LYP	UHF	B3LYP
NTO → **10** + H	70.0	94.6	94.4	72.6	97.7
NTO → **11** + H	76.8	91.8	90.6	69.4	93.4
NTO → **12** + NO_2	43.4	70.3	62.6	42.4	61.1
2 → **14** + NO_2	45.0		64.7	44.1	63.4
2 → **15** + OH	83.9		115.5	83.8	115.0
5 → **13** + OH	−13.8		39.8	−14.4	38.3

[a] Energies are corrected for zero-point vibrational energy using UHF/6-31+G* frequencies scaled by 0.89.

The δ_{NH} and χ_{anis} values in Figure 2 again give the order of aromaticity as **4** > **2** > **3** > **1**. The triazoles are less aromatic than benzene, which possesses a much larger χ_{anis} and perfectly equal carbon−carbon bond lengths. The aromaticity of anions **8** and **9** is difficult to judge based on the NMR shieldings, because the negative charge increases the shielding relative to the neutral structures, but the χ_{anis} values in Figure 2 suggest again that they are more aromatic than **1**. The δ_{NH} and χ_{anis} values for **4** are very similar to those for its unsubstituted analogue **21**, and the δ_{NH} and χ_{anis} values for **3** are similar to those for the unsubstituted analogue **20**. Comparison of the δ_{NH} and χ_{anis} values shows that **20** is less aromatic than **21**, which explains why **21** is the predominant tautomer of 1,2,4-triazole in solution.[38] The series **16**, **17**, and **18** (Figure 2) illustrates the deshielded the N−H proton and large χ_{anis} for the aromatic **16** compared with nonaromatic **17** and **18**. The δ_{NH} value is a poor measure of relative aromaticities for the series **16**, **19**, and **20** because of electronegativity differences. The χ_{anis} values suggest the aromaticities of these three heterocycles are about the same.

(d) Energies for NTO Tautomers. The present study shows that improvement in the theoretical treatment modifies the RHF/6-31G* energy profile for the NTO tautomers and anions obtained in previous work by Ritchie.[8] The estimated energy differences between NTO and its tautomers **2**−**7** are sensitive to the theoretical methods employed (Table 8). Smaller energy differences are obtained with the use of correlated methods. Such behavior is common and has been reported for several parent tautomeric systems. Particularly, both tautomers **2** and **4** have small MP2/6-311+G**+ZPE energy differences with NTO of only 4.4 and 4.7 kcal/mol, respectively (Table 8). However, the related hydroxy tautomer **3** is 11.6 kcal/mol less stable than NTO at this level of theory. Interestingly, the energy difference between the related formamide−formimidic acid tautomers is 11.5 kcal/mol at G2.[39] Tautomers **2** and **4** are evidently stabilized as compared with the parent formamide. We ascribe this to the enhanced aromaticity in these structures. While the same should apply to tautomer **3**, this structure is destabilized because of the repulsion between the neighboring lone pairs on the ring nitrogens N1 and N2. Structure **7** does not have the benefit of aromatic stabilization,[35] and it is less stable (17.7 kcal/mol higher in energy than NTO) than all except the *aci*-nitro tautomers.

The B3LYP method gives larger energy differences than MP2 between the enol tautomers and NTO, with values of 9−10 kcal/mol for **2** and **4**. These are twice as large as those obtained with MP2/6-311+G**. This behavior of B3LYP is opposite to that for the nitromethane tautomers where it gives smaller energy differences than MP2.

We next consider the nitronic acid tautomers **5** and **6**. They have significantly larger energy differences of ca. 30 kcal/mol with NTO although the relative energy of the *aci*-nitro-, hydroxy-substituted triazole **6** varies strongly with the theoretical method employed (Table 8). Of the two tautomers, **6** is favored by 3.9 kcal/mol at MP2/6-311+G**, while the B3LYP method favors **5** by 2.5 kcal/mol. Interestingly, while the amide ⇌ imidic acid tautomerism for the nitro compounds NTO and **2** is in favor of NTO by 4.4 kcal/mol, this energy difference is reversed (at MP2) for its two nitronic acid tautomers **5** and **6**. The fulvene-like skeleton of **6** enables delocalization of the π-system and enhances its stability relative to **5**. The larger π-system delocalization in **6** than in **5** is also evident from the bond length criteria discussed above. At the MP2/6-311+G** level **6** is 28.0 kcal/mol less stable than NTO and 29.7 kcal/mol with B3LYP. We expect this energy difference to be an upper limit. This expectation is based on the observation that more complete treatments of the electron correlation and larger basis sets reduce the energy difference between the nitro and *aci*-nitro tautomers of nitromethane (see Table 4).

Bond Dissociations. Homolytic bond cleavages and hydrogen atom transfers are known to play a role in initiating the decomposition of other nitroaromatic explosives, so we have computed several bond dissociation energies for NTO and its tautomers at the UHF and B3LYP theoretical levels. These results are given in Table 9. Because of the tendency for UHF theory to underestimate bond homolysis energies (see Table 4), the discussion will focus on the B3LYP results.

(a) C−NO_2 Cleavage. At high temperatures, above ca. 900 °C, the most important pathway for decomposition of nitroaromatic explosives is by initial cleavage of the C−NO_2 bond.[27] The B3LYP/6-311+G** bond strength for the C−NO_2 bond in NTO is 61.1 kcal/mol (Table 9). Because the C−NO_2 bond strength in nitromethane is underestimated by 9 kcal/mol at this level of theory (Table 4), our best estimate for the bond energy in NTO is 70 kcal/mol. This seems reasonable when compared to the 71.4 ± 2.0 kcal/mol C−NO_2 bond enthalpy for nitrobenzene, measured using laser induced homolysis in the gas phase.[40]

(b) Hydrogen Atom Transfer. At lower temperatures in the condensed phase intermolecular hydrogen atom transfers play a role in the decomposition of 2,4,6-trinitrotoluene (TNT).[27] Observation of a primary deuterium kinetic isotope effect suggests hydrogen atom transfer is also important in the decomposition of NTO,[41] and Menapace suggested that the NO_2 group in NTO acts as an acceptor in a bimolecular hydrogen atom transfer.[41]

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Our computed bond strengths (Table 9) for the N2−H and N4−H bonds of NTO are respectively 97.7 and 93.4 kcal/mol at the B3LYP/6-311+G** level after correction for zero-point vibrational energies. By comparison, the N−H bond strengths in NH_3, CH_3NH_2, and aniline are respectively 103 ± 3, 92 ± 3, and 80 ± 3 kcal/mol at 298 K.[42]

The N−H bonds of NTO are not unusually weak, but that does not mean hydrogen atom transfers are unimportant. Any reactive radical generated during the decomposition could act as a hydrogen acceptor. The barrier for hydrogen atom transfer is much smaller than the actual bond strength. For example, the C−H bond strengths of CH_4 and CF_3H are both 102 kcal/mol, but the barrier height for hydrogen atom transfer from CH_4 to CF_3 is only 14 kcal/mol.[43]

(c) N−OH Cleavage. In nitroaromatic explosives such as TNT, picramid, and picric acid, a thermally allowed 1,5-hydrogen atom shift leads to formation of the *aci*-nitro tautomers, which can undergo further reactions such as cyclization and N−OH cleavage.[7,27] The 1,5-H shift can take place when a substituent which can donate a hydrogen like CH_3, NH_2, or OH is located ortho to the NO_2 group. The N−OH bond of the *aci*-tautomer is expected to be quite weak, considering the 45 kcal/mol bond strength computed for *aci*-nitromethane (see discussion above). The substituent effect is illustrated by relative rates for decomposition of 2-nitrotoluene, 3-nitrotoluene, and 4-nitrotoluene, which are 400:0.8:2.0 at 200 °C in the gas phase.[27] The fact that TNT self-ignites at 210 °C while 1,3,5-trinitrobenzene is stable at 300 °C is further evidence for the role of the ortho methyl substituent.[27]

It should be recognized here that the *aci*-nitro tautomers are more accessible in other nitroaromatic explosives than in NTO, because in NTO the 1,5-hydrogen shift pathway is not available. However, the high acidity of NTO suggests base-catalyzed tautomerization via anions **8** and/or **9** should be a facile process. Anion **8** could be reprotonated to give **3** or **5**, and **9** could be reprotonated to give **2** or **7**. In addition, double tautomerism can lead to **6** or **4**.

The B3LYP/6-311+G** bond strength for the N−OH bond in **5** is 38 kcal/mol, 10 kcal/mol lower than our estimated N−OH bond strength for *aci*-nitromethane. The low energy suggests N−OH bond cleavage could play a part in the NTO decomposition. Bimolecular hydrogen atom transfer to the NO_2 group[41] could also generate a reactive nitronic acid radical, which would easily undergo subsequent N−OH or C−N cleavage. For the purpose of comparison, we note that the C−OH bond strength for hydroxy tautomer **2** is 115 kcal/mol (Table 9), which is much larger than the N−OH bond energy in **5**.

Conclusions. An important outcome from the present study is our finding that the B3LYP hybrid density functional is an accurate and computationally efficient method for computing energies and geometries on large molecules. Both MP2/6-311+G** and B3LYP/6-311+G** gave satisfactory energies for tautomerization, ionization, and bond dissociations of the small model system, nitromethane. On the other hand, SCF theory is not adequate for our purposes, especially for computing bond dissociation energies. The MP2/6-31+G* and B3LYP/6-31+G* geometries for the NTO anion prove satisfactory when compared with the experimental structure for the diaminoguanidinium salt, and the density functional method gives reasonable harmonic vibrational frequencies for NTO.

We have explained the rather small energy difference between NTO and the hydroxy tautomers **2** and **4** (4 kcal/mol at MP2/6-311+G** and 9 kcal/mol at B3LYP/6-311+G**) as a consequence of enhanced aromaticity in **2** and **4** compared with **1**. The enhanced aromaticity of these 1*H*-1,2,4-triazole systems is evident from calculated C−N bond lengths, chemical shifts of the NH protons, and magnetical susceptibility anisotropies. Likewise, the rather high acidity of NTO is explained in terms of the delocalized, aromatic character of the NTO anions. The computed proton affinity for the NTO anion is a low 321 kcal/mol.

The *aci*-nitro tautomers **5** and **6** are 30 kcal/mol less stable than NTO itself. The difference in stabilities is considerably larger than the 14 kcal/mol difference for the parent tautomeric system nitromethane/*aci*-nitromethane, which is probably a consequence of repulsion between the adjacent nitrogen sp^2 lone pairs in **5** and **6**. However, the *aci*-nitro tautomers are stable enough that they might play a part in the NTO decomposition.

Experimental observations by various groups and the present results do not give definite answers on the question of the NTO decomposition mechanisms. We have suggested that hydrogen atom transfers are likely to play a role in the condensed phase. Cleavage of the $C-NO_2$ bond seems a likely process for initiating the decomposition at high temperatures, but Botcher's recent experimental findings[4e] run counter to this suggestion. Our calculations show that several tautomers of NTO are energetically accessible, and these may play a role in the condensed phase process, where they can be formed by a base-catalyzed mechanism. We have suggested N−OH bond cleavage of the *aci*-nitro tautomer could generate a reactive hydroxy radical in the initial stages of the decomposition.

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Supporting Information Available: Table of bond lengths of NTO tautomers and anions computed at various theoretical levels (3 pages). See any current masthead page for ordering and Internet access instructions.

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