of data collection (2 days). The structure was initially solved by direct methods (using the "hard" option of MITHRIL). This revealed all C and O atoms of the cyclopropenone units, along with the B and two F's. Difference Fourier synthesis revealed the remaining heavy atoms and the disorder in the BF_3 unit. Initial refinements were done with all *F* occupancies at 0.5, giving *R* 0.175. Isotropic refinement of *F* occupancies and all atomic positions for four cycles brought *R* to 0.105. Anisotropic refinement of the B, C, and O positions followed by introduction of aromatic hydrogens at calculated positions brought *R* to 0.071. The fluorine occupancies were then fixed at 0.46 for F1–3 and 0.54 for F11–13 (based on the average values of those sets resulting from the refinement), and the fluorines were refined anisotropically. Difference peaks of 0.2 e/Å^3 between O1 and O2 and O2 and O4 were then identified as hydrogens. Two more cycles of anisotropic refinement of the heavy atoms brought *R* to its final value of 0.049. The linear absorption coefficient being only 0.709 cm^{-1}, no absorption corrections were made.

Intermolecular contacts (Figure 2) involve F---H and H---H contacts at distances approximating the sum of the van der Waals radii of the elements.

Final positional and thermal parameters are given in Table V, observed and calculated structure factors in Table VI, and general temperature factors in Table VII, all in the supplementary material.

Acknowledgment. We gratefully acknowledge indispensable assistance and advice on all aspects of crystallography from Prof. Stephen Koch. We are also grateful to Christopher Pisani for assisting with titrations and spectroscopic studies of **2**.

Supplementary Material Available: Tables of positional and thermal parameters and temperature factor expressions (4 pages); observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

Structures and Energies of the Tautomers and Conjugate Bases of Some 1,2,4-Triazolones[†]

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Molecular orbital calculations at the AM1, 3-21G//3-21G, and 6-31G*//3-21G levels were performed for several possible tautomers of 1,2,4-triazol-5-one and 3-nitro-1,2,4-triazol-5-one. Calculations were also performed at the AM1, 3-21G//3-21G, and 6-31+G//3-21G levels for some conjugate bases of these compounds. The results show the 1*H*,4*H* tautomer to be most stable. 5-hydroxy-1*H*-1,2,4-triazole and 3-nitro-5-hydoxy-1*H*-1,2,4-triazole are found to lie 9.4 and 7.5 kcal/mol, respectively, higher in energy than the corresponding 1*H*,4*H* isomer. It is believed that the calculations may overestimate this relative energy by perhaps 1–3 kcal/mol. The calculations also predict that deprotonation is most likely at N_4 of the lowest energy triazolone, but nearly equally likely at N_1 and N_4 for the corresponding nitrotriazolone (although the N_4 position is slightly favored). We also examined the substitution effects of the nitro group by comparing calculated geometries, relative energies, and electrostatic potentials of the triazolones and nitrotriazolones. Electronegativity effects predominate for the neutral compounds. In the conjugate bases, a significant contribution from resonance participation of the nitro group was found. Finally, we point out some problems in using the electrostatic potential to predict the site of electrophilic substitution in the triazolone.

3-Nitro-1,2,4-triazol-5-one (NTO), although first synthesized some time ago,[1] is now being investigated for use as a less sensitive explosive.[2] It is consequently desirable to determine some of the properties of both NTO and 1,2,4-triazol-5-one (TO), the latter of which yields NTO upon nitration.[3] In particular, we wish to determine the relative energies of the various tautomeric forms and conjugate bases of TO and NTO. In addition, we also examine their calculated electrostatic potentials to determine the use of this quantity for predicting the site of electrophilic attack.

Previous interest in the 1,2,4-triazolones has centered around the possibility of tautomerism[4] and their acidity,[5] which is roughly in the range of carboxylic acids and phenols. Also, other properties and reactions of these compounds have been recently reviewed.[6] Still, the relative energies of the various possible isomeric forms are not known with any certainty. Modern quantum mechanical calculations have proven accurate and useful in predicting these quantities in other system,[7] and so we examined the tautomers (I–VI) and conjugate bases (VII–IX) shown in Chart I using molecular orbital methods. We also examined some nitronic acid tautomers of NTO; these appear as X and XI in Chart I. They might be formed by kinetically controlled protonation of an initially formed conjugate base. (A similar phenomenon has long been suspected to occur with nitromethane and other primary and secondary nitroalkanes.[8])

Each of the forms shown in Chart I is a distinct chemical compound with unique properties, such as impact sensitivity for example. It is important to know their relative

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[†] This work was jointly funded by the U.S. Department of Defense, Office of Munitions, and the Department of Energy.

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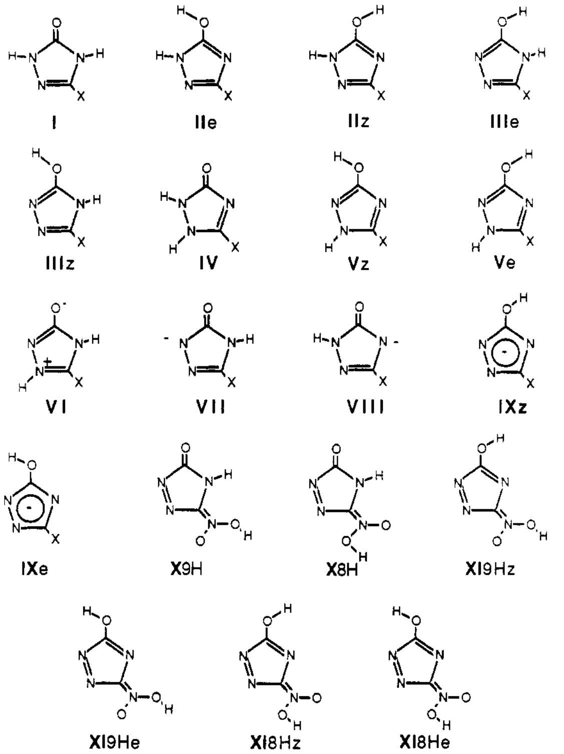
0022-3263/89/1954-3553$01.50/0

Chart I. Structures of the Tautomers and Conjugate Bases Examined in This Paper, X = H and NO_2



energies to determine their possible occurrence in preparing, handling, storing, and decomposing NTO. Although Katritsky and Ogretir assign I, $X = NO_2$, as the structure of NTO,[3c] it is worth noting that the molecular structure of the explosive called NTO has not been definitively determined and, in any case, may depend upon the external environment, be it gas, liquid, solid, solvent of recrystallization, or the presence of adventitious acids and bases. In any case, other forms of NTO may occur as metastable intermediates in its decomposition, which would be desirable to identify.

It is also of quite general interest to determine the effects of substituents in influencing molecular geometry, tautomeric equilibria, and acidities. Thus, comparison of the calculated properties of the tautomeric forms and conjugate bases of NTO (I–IX, $X = NO_2$) with those of the parent triazolone (I–IX, X = H) should prove interesting.

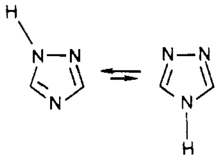
Methods

Standard quantum mechanical calculations were performed with the GAUSSIAN82 computer program.[9] Standard basis sets were used throughout.[10] AM1 calculations[11] were also performed by using MOPAC.[12]

Geometries were optimized in the ab initio calculations using the 3-21G basis set, unless otherwise noted. Final energies were obtained at the 3-21G geometry using the 6-31G* basis set for the various tautomers or the 6-31+G basis set for the conjugate bases. These are denoted 6-31G*//3-21G and 6-31+G//3-21G, respectively. These calculations ignore the effects of electron correlation. For related amide–iminol tautomerism, these effects on the relative energies may be as large as 1–3 kcal/mol, usually favoring the iminol.[13] Also, our neglect of differences in zero-point energies of the tautomers introduces an additional, but in all likelihood small, uncertainty. AM1 calculations were performed with complete geometry optimization, assuming planar geometries. For some species, force constants were obtained by using AM1 with the intention of determining whether the computed structures were in fact minima on the potential energy surface. As described below, these calculations revealed an erroneous tendency of AM1 to favor nonplanar rings in the 1,2,4-triazoles and 1,2,4-triazolones.

Results

1,2,4-Triazoles. Before presenting the results for the species shown in Chart I, it is worthwhile to compare the ab initio and semiempircal methods for a case in which there is readily available experimental data. Thus, calculations were performed for both the *1H* and *4H* tautomers of the parent 1,2,4-triazole, shown in eq 1.


(1)

Results from 6-31G*//6-31G* and AM1 calculations are listed in Table I.

The ab initio results are in good agreement with previous calculations and with experiment. The *1H* isomer is favored by 7.0 kcal/mol at 6-31G*//6-31G*. This result compares with 6.7 kcal/mol found at 6-31G*//3-21G and 3.8 kcal/mol at 3-21G//3-21G.[14] RMP2/6-31G*//6-31G* calculations, shown in Table I also, indicate a negligible effect of inclusion of electron correlation upon the relative energies. In agreement with these results, the *1H*-1,2,4-triazole is the predominant, and frequently only, species observed in both gas and condensed phases.[15]

On the other hand, it can be seen that the AM1 method incorrectly favors the *4H* isomer. It thus appears necessary to add a 12 kcal/mol correction factor to the AM1 H_f of *4H*-1,2,4-triazole, to account for the underestimation of the repulsion between adjacent pyridine-like nitrogens. This correction was required for MNDO also.[16] Moreover, the H_f from AM1 for the triazoles is much too high when compared with the experimental value of 46 kcal/mol.[17]

Vibrational frequency calculations were also performed for the *1H*- and *4H*-1,2,4-triazoles with both ab initio and semiempirical methods. Planar geometries were assumed in both sets of calculations. The planar tautomers are

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Table I. Calculated Quantities for 1*H*-1,2,4-Triazole (A) and 4*H*-1,2,4-Triazole (B) from 6-31G* Basis Set[a]

	A				*B*	
quantity	6-31G*	AM1	X-ray[b]	u-wave[c]	6-31G*	AM1
E_{calc}	−240.804 148	77.0			−240.792 978	72.9
E_{rel}	0.0	0.0			7.0	−4.1
dipole	2.99	2.74			5.95	5.33
$R(N_1–N_2)$	1.341	1.336	1.359	1.381	1.365	1.321
$R(N_2–C_3)$	1.294	1.365	1.323	1.328	1.281	1.362
$R(C_3–N_4)$	1.355	1.407	1.359	1.354	1.735	1.400
$R(N_4–C_5)$	1.297	1.351	1.324	1.280	1.356	1.400
$R(C_5–N_1)$	1.329	1.407	1.331	1.375	1.281	1.362
$R(N–H)$	0.993	0.996			0.993	0.984
$R(C_3–H)$	1.069	1.094			1.069	1.092
$R(C_5–H)$	1.070	1.094			1.069	1.092
$\angle N_1N_2C_3$	102.4	104.6	102.1	102.7	107.5	109.2
$\angle N_2C_3N_4$	115.0	112.7	114.6	113.0	110.4	108.5
$\angle C_3N_4C_5$	102.5	103.6	103.0	106.8	104.4	104.7
$\angle N_4C_5N_1$	110.3	108.9	110.1	109.0	110.4	108.5
$\angle C_5N_1N_2$	109.9	110.3	110.2	108.5	107.5	109.2
$\angle HNC$	129.6	128.7			128.0	127.7
$\angle HC_3N_4$	122.9	122.9			123.7	124.3
$\angle HC_5N_1$	123.4	123.8			125.9	127.3
$k < 0$	0	1			0	0
ZPE	41.0				40.5	
E(RMP2)	−241.559 912				−241.548 420	
E_{rel}(MP2)	0.0				7.2	

[a] Calculated energies in atomic units for 6-31G* and kilocalories/mole for AM1, relative energies in kilocalories/mole, dipole moment in Debye, bond lengths in angstroms, and bond angles in degrees. [b] Reference 15c. [c] Reference 15b.

Table II. Calculated Heats of Formation from AM1 and Total Energies from ab Initio Calculations for the Species Shown in Chart I

	AM1, kcal/mol	3-21G//3-21G, hartrees	6-31G*//3-21G, hartrees	6-31+G//3-21G, hartrees
I, X = H	29.2	−313.907 556	−315.681 762	−315.533 420
I, X = NO_2	43.8	−516.177 889	−519.126 312	−518.868 055
IIe, X = H	42.3	−313.867 390	−315.654 858	
IIz, X = H	37.5	−313.880 536	−315.666 807	
IIz, X = NO_2	52.2	−516.152 316	−519.114 303	
IIe, X = NO_2	57.4	−516.138 348	−519.101 746	
IIIz, X = H	33.6	−313.871 967	−315.653 230	
IIIe, X = H	38.7	−313.856 074	−315.639 245	
IIIz, X = NO_2	45.8	−516.146 078	−519.102 175	
IIIe, X = NO_2	50.7	−516.131 522	−519.089 227	
IV, X = H	51.9	−313.867 805	−315.646 471	
IV, X = NO_2	69.9	−516.137 273	−519.089 165	
Ve, X = H	39.6	−313.873 797	−315.662 162	
Vz, X = H	40.5	−313.874 461	−315.662 457	
Vz, X = NO_2	55.4	−516.144 170	−519.106 900	
Ve, X = NO_2	54.3	−516.144 693	−519.107 190	
VI, X = H	47.3	−313.861 075	−315.638 632	
VI, X = NO_2	61.5	−516.125 133	−519.076 948	
VII, X = H	0.0	−313.295 106		−314.950 519
VII, X = NO_2	−16.0	−515.615 442		−518.335 102
VIII, X = H	2.5	−313.311 082		−314.966 022
VIII, X = NO_2	−2.8	−515.619 228		−518.335 787
IXe, X = H	2.1	−313.288 105		−314.942 267
IXz, X = H	2.2	−313.287 186		
IXe, X = NO_2	−10.2	−515.604 033		
IXz, X = NO_2	−10.4	−515.603 873		−518.322 354
X, 9H	58.2	−516.132 459	−519.064 906	
X, 8H	57.5	−516.135 916	−519.068 439	
XI, 9He	66.4	−516.099 871		
XI, 9Hz	66.5	−516.101 642	−519.054 572	
XI, 8Hz	66.7	−516.101 343		
XI, 8He	67.0	−516.099 043		

verified to be minima on the 6-31G*//6-31G* potential energy surface, as was the case at 3-21G//3-21G.[16d] In contrast, AM1 shows the planar 1*H* isomer as a transition state, while the planar 4*H* isomer is a minimum. The minimum obtained for the 1*H* isomer from the AM1 calculations has a pyramidal nitrogen that is only 0.5 kcal/mol lower in energy than the form shown in Table I. Experimental data support a planar structure, and it must be concluded that the tendency for nitrogen to pyramidalize is overestimated in the AM1 method. This tendency extends to the triazolones, where nonplanar distortions occurred in a number of cases when planarity was not explicitly enforced.

1,2,4-Triazolone Tautomers. Table II shows the calculated energies of the 1,2,4-triazolone tautomers I–VI. Table III lists their relative energies from the various computational models, while Table IV lists some optimized geometrical parameters.

Compound I is found to be the most stable isomer at all levels of theory and irrespective of nitro group substitution.

Table III. Relative Energies for I-VI (kcal/mol) from the Indicated Computational Models

	AM1		3-21G//3-21G		6-31G*//3-21G	
structure	X = H	X = NO_2	X = H	X = NO_2	X = H	X = NO_2
I	0.0	0.0	0.0	0.0	0.0	0.0
IIe	13.1	13.6	25.2	24.8	16.9	15.4
IIz	8.3	8.4	17.0	16.0	9.4	7.5
IIIe	9.5	6.9	32.3	29.1	26.6	23.3
IIIz	4.4	2.0	22.3	20.0	17.9	15.1
IV	22.7	26.1	24.9	25.5	22.1	23.3
Vz	11.3	11.6	21.2	21.2	12.3	12.2
Ve	10.4	10.5	20.8	20.8	12.1	12.0
VI	18.1	17.7	29.2	33.1	27.1	31.0

Table IV. Some Optimized Geometrical Parameters for I-VI[a]

description	I	IIe	IIz	IIIe	IIIz	IV	Vz	Ve	VI
$R(N_2-C_3)$									
X = H, AM1	1.342	1.364	1.365	1.360	1.358	1.399	1.400	1.402	1.364
X = H, 3-21G	1.277	1.302	1.302	1.287	1.284	1.351	1.338	1.341	1.293
X = NO_2, AM1	1.360	1.382	1.384	1.383	1.382	1.407	1.412	1.413	1.380
X = NO_2, 3-21G	1.266	1.294	1.294	1.277	1.276	1.336	1.330	1.327	1.285
$R(C_3-N_4)$									
X = H, AM1	1.409	1.408	1.405	1.406	1.406	1.337	1.350	1.353	1.371
X = H, 3-21G	1.379	1.377	1.380	1.384	1.386	1.285	1.311	1.310	1.327
X = NO_2, AM1	1.422	1.424	1.420	1.420	1.420	1.348	1.369	1.372	1.389
X = NO_2, 3-21G	1.364	1.356	1.360	1.370	1.370	1.265	1.294	1.296	1.322
$\angle N_2C_3N_4$									
X = H, AM1	111.2	113.7	113.5	109.1	109.0	113.0	109.8	110.0	106.7
X = H, 3-21G	112.5	115.1	114.8	110.8	110.6	114.1	110.0	110.5	107.5
X = NO_2, AM1	111.4	113.6	113.4	109.2	109.2	113.4	109.8	110.2	107.0
X = NO_2, 3-21G	114.3	116.7	116.3	112.4	112.3	116.7	112.5	111.9	109.1

[a] Bond lengths in angstroms, angles in degrees. Additional parameters are available as supplementary material.

Table V. Atom Equivalents Used in Calculating the Heat of Formation of NTO

atom type and number	3-21G equivalent, hartrees	6-31G* equivalent, hartrees
SUM	−516.15701	−519.12114
E_{calc}	−516.17781	−519.12631
H_f(g), kcal	−13.1	−3.2
H_f(C), kcal from eq 2	−37.8	−26.7

This is in agreement with the findings of Katritsky and Orgetir. The heat of formation of I, X = NO_2, can be estimated from the ab initio energies by using the group equivalents of Ibrahim and Schleyer.[18] Table V shows the result of this calculation. The 6-31G*//3-21G calculations are our best and yield a H_f(g) and −3.2 kcal. The heat of formation obtained in this manner is appropriate for the gas phase. Measurements are, however, commonly made in the solid phase. We frequently use 20 kcal/mol as an estimate of the heat of sublimation of "normal" organic compounds. Alternatively, gaseous and condensed phase heats of formation can be related using the purely ad hoc correlation shown in eq 2 that we have previously devised.[19]

$$H_f(c) = 1.13H_f(g) - 23.03 \qquad (2)$$

$$N = 23, r = 0.987, SD = 4.4 \text{ kcal}$$

Use of eq 2 with the 6-31G*//3-21G H_f(g) yields a H_f(c) of −26.7 kcal, our preferred result. This value is close to that reported experimentally,[20] as shown in Table V. The AM1 H_f for I, X = NO_2, shown in Table II, is seriously in error, even after systematic corrections of −10 kcal/mol are made for the presence of the CNO_2 group, as previously recommended.[19]

Although I is the most stable isomer examined, Table III shows that other forms exist as well. The relative energies show a significant basis set effect in the ab initio calculations, but the ordering is the same with both basis sets. The larger basis gives systematically smaller energy differences relative to I, irrespective of the substituent, and are the preferred results. AM1 and the 6-31G*//3-21G relative energies are quite similar, except for III and VI; III has adjacent pyridine-like nitrogens and thus should probably be "corrected" as suggested above for the 4*H*-1,2,4-triazole. Adding 12 kcal/mol to the relative energy of III to AM1 yields 16.4 and 14.0 kcal/mol for III, X = H, NO_2, respectively. These "corrected" final relative energies are in close agreement with the 6-31G*//3-21G results. The reasons for the discrepancy in the relative energy of VI with the two methods is not known. Thus, with the above considerations, the AM1 and the 6-31G*//3-21G stability ordering begins I > IIz > V > IIIz. The 6-31G*//3-21G calculation finish with V > VI, while AM1 predicts the opposite. Hence there is a good deal of agreement between the methods as to the relative ordering.

Two additional observations may be made regarding the data in Table III. First, in addition to the rank ordering given above being the same whether X = H or X = NO_2, the relative energies are also quite independent of the nature of X. Only a few differences exceed 2 kcal/mol, and in the mesoionic VI this seems quite reasonable. Second, there are relatively large energy differences between C–O bond rotamers in II and III, with the favored position of the hydroxylic hydrogen being nearer the sp^2 nitrogen. When both nitrogens are sp^2, as in V, there is little preference between the rotamers. This is in keeping with the operation of the generalized anomeric effect.[21]

The geometrical parameters shown in Table IV and supplementary material demonstrate some interesting

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Table VI. Energies of the Indicated Conjugate Base plus a Proton Relative to I (kcal/mol) from the Various Computational Models

	AM1[a]		3-21G//3-21G[b]		6-31+G//3-21G[b]	
structure	X = H	X = NO_2	X = H	X = NO_2	X = H	X = NO_2
VII	336.7	306.1	384.3	352.9	365.8	334.4
VIII	339.2	319.3	374.3	350.6	356.0	334.0
IXe	338.8	326.5	388.7	360.1	371.0	342.4
IXz	338.9	326.3	389.3	360.2		

[a] The H_f of the proton was taken as 365.9 kcal/mol in the AM1 calculations, which is equal to the observed H_f of the hydrogen atom plus its ionization potential. [b] Ab initio results do not include differences in zero-point energies, which would reduce the relative energies by about 8 kcal.

Table VII. Some Optimized Geometrical Parameters for VII–IX[a]

description	VII	VIII	IXe	IXz
R(N_1–N_2)				
X = H, AM1	1.314	1.347	1.299	1.300
X = H, 31-21G	1.443	1.433	1.425	1.429
X = NO_2, AM17	1.268	1.328	1.273	1.274
X = NO_2, 3-21G	1.347	1.408	1.385	1.387
R(N_2–C_3)				
X = H, AM1	1.355	1.362	1.391	1.391
X = H, 3-21G	1.281	1.308	1.318	1.317
X = NO_2, AM1	1.405	1.382	1.422	1.422
X = NO_2, 3-21G	1.381	1.297	1.317	1.317
R(C_5–N_1)				
X = H, AM1	1.416	1.453	1.410	1.404
X = H, 3-21G	1.347	1.390	1.317	1.312
X = NO_2, AM1	1.459	1.467	1.434	1.429
X = NO_2, 3-21G	1.404	1.402	1.336	1.334
R(C_5–O)				
X = H, AM1	1.263	1.263	1.389	1.389
X = H, 3-21G	1.247	1.241	1.379	1.380
X = NO_2, AM1	1.252	1.257	1.383	1.382
X = NO_2, 3-21G	1.225	1.231	1.365	1.365

[a] Bond lengths in angstroms, angles in degrees. Additional information available as supplementary material.

Table VIII. Comparison of Calculated Bond Lengths in VII, X = NO_2, and Those Observed in the Ethylenediamine Salt of NTO[a]

bond	obs[b] (av)	calc	error
C_5–O	1.276, 1.257, 1.260 (1.264)	1.231	−0.033
N_1–N_2	1.370, 1.359, 1.363 (1.364)	1.408	+0.044
N_2–C_3	1.304, 1.307, 1.307 (1.306)	1.297	−0.009
C_3–N_4	1.337, 1.333, 1.338 (1.336)	1.331	−0.005
N_4–C_5	1.356, 1.357, 1.354 (1.356)	1.373	+0.017
C_5–N_1	1.358, 1.364, 1.362 (1.361)	1.402	+0.041
C_3–(NO_2)	1.451, 1.450, 1.449 (1.450)	1.436	−0.014
N–O	1.228, 1.216, 1.220 (1.221)	1.250	+0.029
N–O	1.219, 1.237, 1.222 (1.226)	1.239	+0.013

[a] Three molecules occur in the asymmetric unit. The geometries of these molecules differ only slightly and are averaged to obtain a value, shown in parentheses, for comparison with the calculations. [b] Reference 24.

systematic differences with X = H and X = NO_2. In the 3-21G//3-21G calculations, the N_1–N_2, N_2–C_3, C_3–N_4, and C_5–O bonds are always shorter while the C_5–N_4 bond is always longer with X = NO_2 than with X = H. R(C_5–N_1), which is the ring bond most distant from the substitution site, shows changes in both directions. Systematic changes are also found in ring angles. The ring angle at C_3 is always larger when X = NO_2. Similarly, the interior angle at N_1 is always larger in the nitro derivatives, but by a smaller amount. Interior ring angles at N_2, N_4, and C_5 are always smaller when X = NO_2.

The AM1 geometries also show interesting systematic effects of substitution, although in a different way than the ab initio ones. With X = NO_2, the bonds about C_3 are always longer, as is the C_5–N_1 bond; the N_1–N_2 bond is always shorter. The remaining ring bond is always shorter with X = NO_2, with the exception of IV. The C–O bond is always shorter with X = NO_2, except in VI. The interior ring angles vary both ways over a small range at C_3, while they are always lesser at N_2 and N_4, but larger at N_1 and C_5 when X = NO_2.

The electrostatic potentials of I, X = H and X = NO_2, obtained at the 6-31G*//3-21G level are shown in Figure 1. The plane illustrated is 1.8 Å above the molecular plane. A comparison of the value of the electrostatic potential over each of the common atoms of TO and NTO shows that the values in NTO are always more positive. It can also be seen that the most negative potentials are associated with the carbonyl oxygen in both cases. Another negative site appears with N_2 of TO, but this region is positive in NTO, where other negative potentials appear near the nitro oxygens. Finally, in NTO a large positive potential is observed over the C–NO_2 bond. This feature is commonly observed in other nitro group containing compounds.[22]

Conjugate Bases. Table VI shows the energies of VII–IX relative to I. Comparison of results from the different methods reveals significant differences. The 6-31+G//3-21G level is believed to be most accurate. At this level VIII is the most stable form for the conjugate base for both X = H and X = NO_2. In contrast, AM1 predicts VII is more stable, whether X = H or NO_2. It can be seen, however, that a correction of 12 kcal/mol to account for the lone pairs of electrons on adjacent nitrogens in AM1, as discussed above, would bring the semiempirical and 6-31G+//3-21G results into qualitative agreement.

Because of the nearly equal relative energies of VII, X = NO_2, and VIII, X = NO_2, both or either may be present under any given appropriate set of circumstances. Initially, alkylation of NTO with dimethyl sulfate or methyl iodide in alkaline medium (1 equiv of base) was reported to yield exclusively substitution at N_4,[23] which, according to the calculations, is the thermodynamically favored deprotonation site. In a latter report[24] the monosodium salt of NTO reacted with dimethyl sulfate to yield two monosubstituted products, corresponding to reaction at N_1 or N_4. In excess alkali, a disubstituted product is formed. These results are consistent with comparable acidities of the proton at N_1 and N_4.

We can also compare the calculated geometry of VIII, X = NO_2, at 3-21G, shown in Table VII, with that of the conjugate base of NTO found in its ethylene diamine salt,[25] which shows deprotonation at the 4-position. Table VIII

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(22) Politzer, P.; Laurence, P. R.; Abrahmsen, L.; Zilles, B. A.; Sjoberg, P. *Chem. Phys. Lett.* **1984**, *111*, 75.

(23) Chipen, G. I.; Bokaldere, R. P. *Khimi. Geterotsik. Soedin.* **1969**, *5*, 159.

(24) Korkman, T. P.; Pevzner, M. S.; Shukova, L. N.; Kravchenko, T. A.; Frolova, G. M. *Zh. Organich. Khimii* **1979**, *16*, 420.

(25) Cromer, D. T.; Hall, J. H.; Lee, K.-Y.; Ryan, R. R. *Acta Crystallogr. C*, in press.

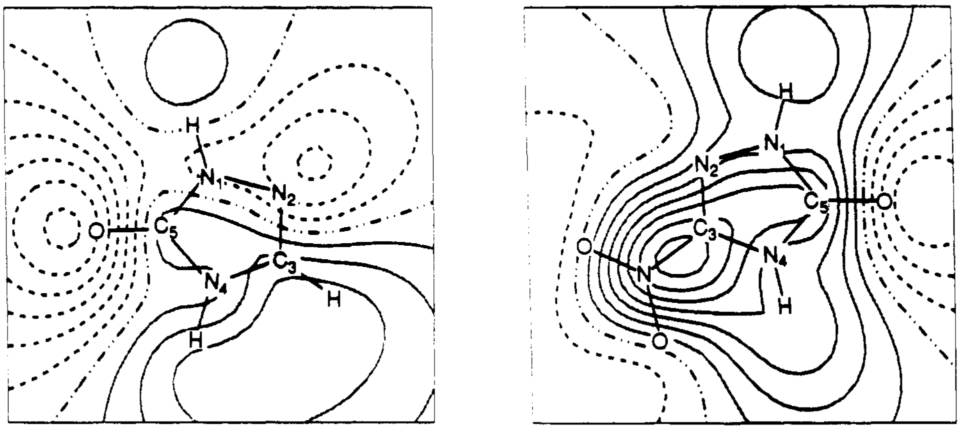
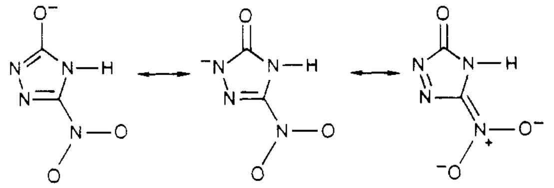


Figure 1. Electrostatic potential (kcal/mol/e) for I (X = H, left panel; X = NO_2, right panel). The illustrated plane is 1.8 Å above the molecular plane. Positive values are indicated with unbroken lines, negative values by dashed lines, and zero as a value by the chain-dashed line. The increment between contours is constant at 5 kcal/mol/e.

shows the relevant comparison. In general, considering the possible effects of crystal environment and limitations of the theory, the geometries agree about as well as can be expected, the maximum deviations being +0.044 and −0.033 Å. The average unsigned error in bond length is 0.023 Å, which is typical for calculations at this level.[26]

It is interesting to determine the effect of nitro group substitution in the conjugate base. At the 6-31+G//3-21G level, our most accurate model, the energy difference between X = H and X = NO_2 for VII, VIII, and IX is quite large. The relevant energy differences being about −30 kcal/mol for VII and IX, but only −22 kcal/mol for VIII. This change in the relative energies brought about by the nitro group is much larger than that found in the neutral tautomers. Thus, the nitro group exerts a strongly stabilizing effect on the conjugate base. The effect is larger at the 1-position than at the 4-position, despite its being more distant, but the N_4 proton is still more acidic than the one at N_1.

The larger effect of the nitro group in VII is clearly the result of resonance participation by the nitro group, as shown below. Similar structures cannot be drawn for VIII.



The resonance effects of the nitro group are clearly manifested by comparing the ring geometry of VII with X = H and X = NO_2. As shown in Table VII, both AM1 and the ab initio calculations indicate shorter C_5–O and N_1–N_2 bonds along with longer C_5–N_1 and N_2–C_3 bonds when X = NO_2. The results are explained by a lessened contribution of the left-hand structure accompanied by an increase of importance in the right-hand structure. The latter structure shows increased double bond character in the shorter bonds and increased single bond character in the longer bonds over that in the former. Further evidence of the importance of nitro group resonance is found by comparing the geometry of the nitro groups in VII and VIII. The C_3–NO_2 bond is shorter in VII while the N–O bonds are longer, as expected.

Nitronic Acids. In addition to the tautomers I–VI, X = NO_2, there also exist a number of possible nitronic acid tautomers for NTO. The calculated energies for these tautomers, X and XI, are shown in Table I, while their energies relative to I, X = NO_2, are shown in Table IX. There are significant differences between each level of theory. The absolute and relative energies of these compounds with AM1 may need correcting, to account for the adjacent nitrogens with eclipsing sp^2 lone pairs of electrons. Thus, although AM1 indicated these isomers are not terribly high in energy, in ab initio results show significantly larger relative energies. In view of the problems of AM1 with this type of compound, the ab initio results seem preferable. With either basis, these nitronic acids are quite high in energy, above I–VI.

Table IX. Energies Relative to I, X = NO_2 (kcal/mol), from the Indicated Computational Models for the Nitronic Acid Tautomers

structure	AM1	3-21G//3-21	6-31G*//3-21G
VII, 9H	14.4	28.5	38.5
VII, 8H	13.7	26.3	36.3
VIII, 9Hs	22.6	47.8	
VIII, 9Ha	22.7	49.0	45.0
VIII, 8Hs	22.9	49.5	
VIII, 8Ha	23.2	49.5	

Discussion

Computational Methods. Throughout the above, a number of corrections were required to the AM1 method. Although such corrections are well justified, the ab initio results did not require such ad hoc adjustments and were in all cases in good agreement with experimental evidence, when it was available. Consequently, further discussion will be limited to results from the 6-31G*//3-21G or 6-31+G method for negatively charged species, which are our preferred results. The AM1 calculations were justified, however, in that they were used to provide starting geometries and force constants for the ab initio calculations. The semiempirical results were also helpful in preliminary scans of the potential energy surface, allowing us to explore more fully than otherwise would have been possible.

Stability Ordering. The three tautomeric equilibria shown in eq 3–5 illustrate some relevant chemical considerations in thinking about the tautomerism of the triazolones. Equation 3 illustrates formamide–formimidic acid tautomerism. In contrast to the commonplace formamide, formimidic acid has not been observed experimentally and is calculated with large basis sets to be about 12 kcal/mol less stable than formamide.[13a] The energy difference in eq 4 has been estimated by ICR measurements to be 7.3 kcal/mol, favoring the amide form.[27]

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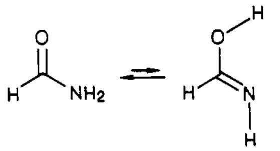
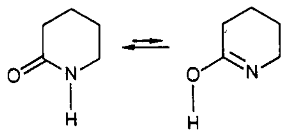
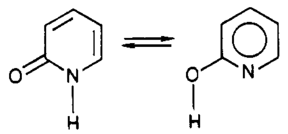
[26] See: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; Chapter 6.



(3)



(4)



(5)

Thus, the amide tautomer is normally the favored form in the absence of other factors. On the other hand, 2-pyridone and 2-hydroxypyridine (shown in eq 5) coexist in the gas phase, and energy differences of –0.8 kcal/mol[28] and –0.6 kcal/mol[29] (favoring the hydroxy form) have been determined from experimental measurements. But this equilibrium is sensitive to environmental effects, and 2-pyridone frequently predominates, sometimes exclusively, in condensed phases.[30] In agreement with these observations, large-scale calculations indicate that only a few tenths kcal/mol separate these tautomers,[13a] although the ordering is not correct unless electron correlation, large basis sets, and zero-point energy differences are properly accounted for. Thus, it is because of the small single molecule energy difference between 2-pyridone and 2-hydroxypyridine that the observed proportions of the two is quite sensitive to environmental effects.

These results, along with a consideration of the discussion accompanying eq 1, above, provide insights to the stability ordering of the tautomers shown in Table III. Thus, I is favored over IIz and V by amounts (7.5 and 12.0 kcal/mol, respectively) corresponding quite closely to the energy differences found in eq 3 and 4 of 12 and 7 kcal/mol, respectively; V apparently suffers unfavorable 1,3-interactions of the hydroxy oxygen and ring sp^2 nitrogens, resulting from lone pair–lone pair repulsions. These repulsions are relieved in IIz, resulting in its greater stability. After V, next most stable is III, where the intrinsic energy differences between 1*H*- and 4*H*-1,2,4-triazoles of about 7 kcal/mol is nearly the same as the energy difference between corresponding forms of IIz and III. Hence, III is less stable than IIz or V because it is a 4*H*- rather than a 1*H*-1,2,4-triazole. Compound IV contains unfavorable adjacent nitrogens and is therefore less stable yet. Compound VI is mesoionic and highest in energy, at least in the gas phase. This energy difference is expected to be quite sensitive to environmental effects.

The correspondence between the relative energy of I and IIz with that found in eq 3 and 4 is quite interesting. If IIz were significantly more aromatic than I, it would have been favored. For example, with 2-hydroxypyridine, the increased resonance stabilization arising from formation of the pyridine ring outweighs the intrinsic stability of the amide based on relative C=O/C—O, C—N/C=N, and N—H/O—H bond strengths. Thus, I must be nearly as aromatic as IIz, the unsubstituted parent of which has been estimated to enjoy between 20–43 kcal/mol of resonance stabilization.[31] The aromatic character of the triazolones is of course evidenced experimentally in that I, X = H, undergoes nitration to form I, X = NO_2.

The stability ordering shown in Table III is pertinent to gas-phase equilibria at low concentrations. As noted above, medium and concentration effects can be quite significant, if the intrinsic relative energy differences are relatively small. Nonetheless, I is calculated to be favored by an amount large enough that it should be present either solely or in easily detectable amounts. Structure II is only slight less stable and, as mentioned above, our neglect of electron correlation and zero-point energy differences would tend to decrease the energy difference by about 1–3 kcal/mol. Thus, it is quite possible that IIz (IIz, X = NO_2, in particular), may be detectable or its existence inferred by experimental techniques, especially in condensed phases. The other tautomers higher in energy appear too unstable to be present in sufficient quantities to be observable, except under nonequilibrium conditions or as reactive intermediates.

Effects of Nitro Group Substitution. Comparison of nitro group effects in I–VI with those in VII–IX reveal two significantly different modes of interaction. In the neutral tautomers, the nitro group had a relatively small effect upon the relative energies, the largest effect being 4 kcal/mol in VI. In this structure, positive charge is localized near the nitro group, and it is not surprising that the electron-withdrawing nature of the nitro group leads to a detectable destabilization relative to X = H. Although the substituent effect of the nitro group was small when measured by the relative energies of I–VI, systematic effects were found in their geometries. The shortening of the ring bonds and opening of the angle at C_3 upon substitution of H by NO_2 is most easily explained by the large electronegativity of the nitro group. The greater electronegativity of NO_2 results in increased withdrawal of charge from the orbital directed at it. This causes greater p character in that orbital and correspondingly less p character in the other orbitals of that atom, causing the ring bonds to shorten and the ipso angle to increase. Similar effects have been observed in substituted benzenes.[32] We have also previously noted that resonance participation of the nitro group in ground state, neutral, closed-shell molecules is smaller than commonly assumed.[33]

In the conjugate bases, there were two major effects of the nitro group, which leads to the greater acidity of nitrotriazolone over that of triazolones. First, there was clear evidence of resonance participation by the nitro group in VII. Large energetic consequences and consistent geometry changes were found. It was also found that the resonance effect led to larger stabilization at the more distant N_1 than at N_4. Second, the electronegativity effect or inductive effect of the nitro group plays an important role in stabilizing VIII, X = NO_2, over VIII, X = H. In VIII, X = NO_2, simple resonance structures cannot be drawn that place the negative charge on the nitro group, and resonance participation of the nitro group is minimal. It is worth noting, however, that the differences of relative energy between VIII, X = NO_2, and VIII, X = H, of –22

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(27) Cook, M. J.; Katritzky, A. R.; Taagepera, M.; Singh, T. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 6048.

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(30) See: Beak, P. *Acc. Chem. Res.* **1977**, *10*, 186 and references therein.

(31) See: Cook, M. J.; Katritzky, A. R.; Linda, P. *Adv. Heterocycl. Chem.* **1974**, *17*, 255.

(32) (a) Trotter, J. *Tetrahedron* **1960**, *8*, 13. (b) Bock, C. W.; Trachtman, M.; George, J. *J. Mol. Struct.* **1985**, *122*, 155 and references therein. (c) George, P.; Bock, C. W.; Trachtman, M. *J. Mol. Struct.* **1986**, *137*, 387.

(33) (a) Ritchie, J. P. *Tetrahedron* **1989**, *44*, 7465. (b) Ritchie, J. P. *J. Am. Chem. Soc.*, in press.

kcal is much larger than the difference in solution pK_a's of I, X = H and X = NO_2, would indicate (pK_a's: I, X = NO_2, = 3.63; I, X = 9.11).[5]

Electrostatic Potentials. It has frequently been claimed that electrostatic potentials can serve as a guide in predicting sites of electrophilic attack.[34] The electrostatic potential for TO, shown in Figure 1, illustrates some of the problems that can occur with this approach. Thus, C_3 has the most positive potential associated with it of any atom in TO and, on this basis, would be expected to be least susceptible to electrophilic attack. Yet, this is the observed site of nitration. Consequently, the electrostatic potential is of no value in predicting the position of nitration in TO.

Electrostatic analysis, of course, only suggests the position an incoming electrophile would initially approach, without any rearrangement of electronic charge. Thus, electrophiles would be expected to approach the carbonyl oxygen or possibly N_2 of TO at first, as these sites have the most negative potentials. Likewise, the most negative site in nitrobenzene is associated with the nitro oxygen,[35] and this would then be the site most attractive initially to an incoming electrophile; yet nitration of nitrobenzene yields *m*-dinitrobenzene. In this latter case, it is well-established (especially in low-temperature NMR studies) that the site of protonation of nitrobenzene is on the nitro oxygen, rather than at the meta carbon to form a Wheland intermediate.[36] If we can assume that a proton and nitronium ion interact in similar ways with the substrate, this suggests that electrophilic attack at O may well be kinetically favored, but that the meta-substituted products normally recovered correspond to the thermodynamically favored product. We assume a similar situation occurs in the nitration of TO. More rapid attack at the oxygen or ring nitrogens results in thermodynamically unstable products, which either readily revert to reactants or rearrange to the observed products at the reaction temperature. Indeed, transformations of aromatic nitramines to nitroanilines are well known.[37] Similarly, nitric acid nitration of pyrazoles yields *N*-nitropyrazoles, which rearrange to *C*-nitropyrazoles upon heating.[38]

The electrostatic potential of NTO is also shown in Figure 1. The electron-withdrawing effect of the nitro group is demonstrated by the potential above the triazole ring being everywhere more positive in NTO than in TO. It should also be noted the the potential over N_1 is less positive than that over N_4, even though the electron pair associated with N_1 could delocalize onto the nitro group, leaving a formal positive charge on N_1, which would lead to large positive potentials. This provides further evidence of the lack of importance of resonance effects and predominance of electronegativity effects in this molecule.

Conclusions

Ab initio calculations were found to provide reliable results in this paper. These show that the 1*H*,4*H* isomer is the most stable form of both 1,2,4-triazolone and 3-nitro-1,2,4-triazolone. The 5-hydroxy-1,2,4-triazole and 3-nitro-5-hydroxy-1,2,4-triazole forms are sufficiently stable that it may be possible to observe them directly or infer their existence under normal conditions. The calculations also showed that deprotonation is easier from N_4 than N_1, although when X = NO_2 the energy difference is quite small.

The effect of nitro group substitution was found to be relatively small, but detectable, in neutral compounds, but quite large in negatively charged species. Electronegativity effects predominate in neutrals, while resonance effects are important in charged species.

Finally, the electrostatic potential was shown not to predict the site of nitration in 1,2,4-triazolone. The resulting 3-nitro-substituted product probably arises as a result of thermodynamic control of the reaction.

Supplementary Material Available: Tables of optimized geometrical parameters for compounds I–IX (9 pages). Ordering information is given on any current masthead page.

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