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MOLECULAR MODELS FOR EXPLOSIVES: APPLICATIONS TO NTO

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MOLECULAR MODELS FOR EXPLOSIVES: APPLICATIONS TO NTO

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We calculated structures and energies for several isomers of 3-nitro-1,2,4-triazol-5-one (NTO), using molecular orbital theory. The 1H,4H isomer was found to be lowest in energy. We predict the existence of an additional low-lying form that may either be directly observable or have its existence inferred in experiments. We also calculated some possible forms of the conjugate base of NTO. Finally, we have applied a new method of calculation to predict the geometry of the diaminoguanidinium salt of NTO.

INTRODUCTION

Advances in computer technology and computational algorithms have enabled accurate molecular orbital calculations to be performed for molecules the size of some common HE's. These calculations provide fundamental molecular properties and can serve as a useful adjunct to experiment in trying to understand the behavior of explosives. Our long term goal is to determine the relationships between the fundamental properties of explosives and their observed behavior. This paper reports some of our results for the explosive 3-nitro-1,2,4-triazol-5-one (NTO).[1] Our results demonstrate what levels of theory are required to obtain accurate predictions.

Among the properties that one would like to know are: molecular structure, energy, and spectroscopic constants, reactivity, and intermolecular interactions. The molecular structure, energy, and spectroscopic constants are useful for determining the thermodynamic properties and establishing the identity of a proposed compound or reactive intermediate. These quantities are becoming increasingly important as spectroscopic investigations are performed with the intention of determining decomposition mechanisms in energetic materials. Thus, comparison of observed spectra with calculated spectra for specific species can help to identify reactive intermediates. Reactions and reactivity of explosives are obviously of great concern. Likewise, intermolecular interactions are important in determining crystal structures.

METHODS

Quantum mechanical calculations reported in this paper were performed with the GAUSSIAN82 computer program.[2] Standard basis sets were used throughout.[3]

RESULTS

Figure 1 shows the structure usually drawn for NTO as I, however, hydrogens on amide nitrogens are frequently quite labile and mobile. Various tautomers of NTO that are difficult to distinguish experimentally from one another and from NTO may thus be formed by possibly facile rearrangements of hydrogens. Other possible tautomers are shown as II-IV in Figure 1. With the available experimental data, it is difficult to establish with certainty that the explosive we commonly refer to as NTO has, in fact, structure I. Although X-ray data has been obtained[4] and may strongly support structure I, the definitive neutron structure has not yet been obtained. Consequently, ab initio molecular orbital calculations were performed to determine the structures and relative energies of NTO and its tautomers.

Table I shows the energies calculated for I-IV at the various levels of theory employed. Energies obtained from the AM1 method,[5] which is superior to MINDO/3 in some regards, are also included for comparison. These energies are seen to wildly disagree.

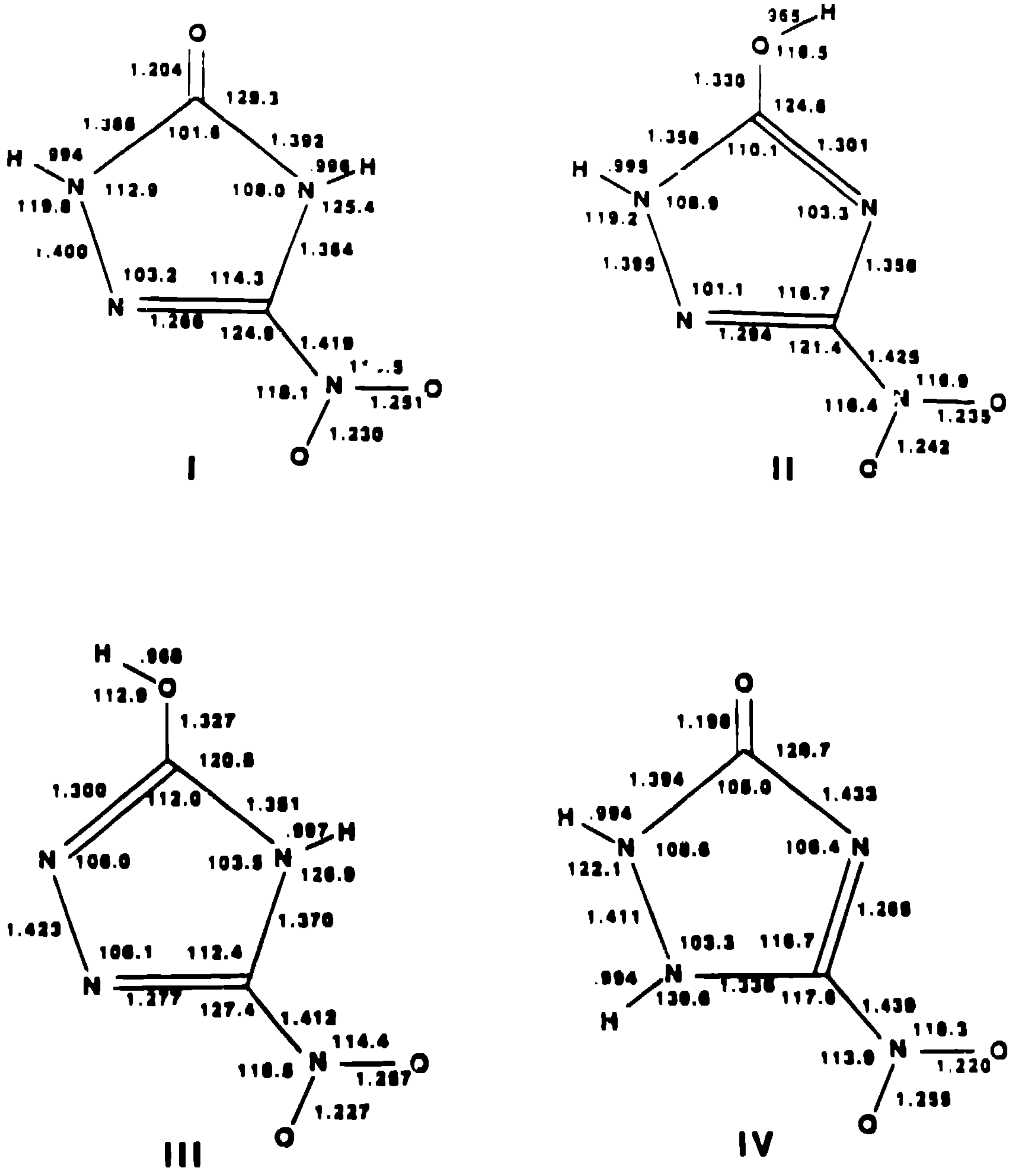


FIGURE 1 OPTIMIZED GEOMETRIES OBTAINED FROM 3-21G CALCULATIONS

TABLE I. CALCULATED ENERGIES OF NTO AND ITS TAUTOMERS FROM VARIOUS LEVELS OF THEORY

Method	I	II	III	IV
MINDO/3 (kcal)	-91.4	-88.1	-92.6	-72.5
AM1 (kcal)	43.8	52.2	45.8	69.9
3-21G//3-21G (au)	-516.17789	-516.12835	-516.14608	516.13727
6-31G*//3-21G (au)	-519.12631	-519.10175	-519.10217	-519.08916
Dipole (D)	1.25	8.6	5.4	6.3

Our best calculations, at 6-31G*//3-21G, indicate that I is the correct structure of NTO. II-IV lie somewhat higher in energy, but conceivably could play a role in solution because they may be energetically accessible. In addition, II-IV have a larger dipole moment than does I and polar solvents may preferentially stabilize II-IV due to solvation differences.

A heat of formation of NTO can be estimated using the calculated energies and atom equivalents of Ibrahim and Schleyer developed for this purpose.[5] Table II shows the result of this calculation. The 6-31G*//3-21G calculations are our best and yield a $H_f(g)$ = 3.2 kcal.

The heat of formation obtained by this method is appropriate for the gas phase. Measurements are, however, commonly made in the solid phase. These quantities can be related using the ad hoc correlation we have previously devised.[illegible] The relationship is shown in Equation 1

$$H_f(c) = 1.13 \bullet H_f(g) - 23.03 \qquad (1)$$

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

quantities in kcal

Use of Equation 1 with the 6-31G*//3-21G $H_f(g)$ yields a $H_f(c)$ of 26.7 kcal, our preferred result.

TABLE II. ATOM EQUIVALENTS AND CALCULATED HEAT OF FORMATION OF NTO.

Atom Type and Number	3-21G Equivalent	6-31G* Equivalent
O_d-(C)	-74.36505	-74.79644
2 C_d $(C_d)(C)_2$	2(-37.66998)	2(-37.88371)
2 N $(H)_2(CO)$	2(-54.17266)	2(-54.46869)
N_d $(H)(C_d)$	-54.13350	-54.45209
N_d $(C)(O_d)(O_s)$	-54.09780	54.44017
O_s (N)	-74.38389	74.79848
O_d (N)	74.36505	74.79644
2 H (N)	2(00.56322)	2(00.56636)
SUM	516.15701	519.12114
Calc. E	516.17781	519.12631
$H_f(g)$ in kcal	13.1	3.2
$H_f(c)$ in kcal from Eq. 1	37.8	26.7

CALCULATED STRUCTURES AND ENERGIES FOR THE CONJUGATE BASES OF NTO

Initial calculations were performed with the 3-21G basis set.[illegible] Geometries were completely optimized assuming the molecules to be planar. Because anions are better described with diffuse functions, additional calculations were also performed using the 6-31G+ basis set[illegible] at the 3-21G geometry. The two sets of calculations are then conveniently denoted as 3-21G//3-21G and 6-31G+//3-21G, respectively.

The structures and energies of the three forms of the conjugate base of NTO were obtained and are shown in Figure 2. Table III shows the calculated total energies for V-VII and the energy of I for comparison. The calculated energies of V-VII show V to be the most stable form. The preference for V is quite small, however, at the 6-31+G//3-21G level.

The calculations agree with the recent crystal structure of the ethylene diamine salt of NTO, which shows deprotonation at the 4 position. Table IV compares the calculated structure of V with that observed for the ethylene diamine salt of NTO. In general, considering the possible effects of crystal environment and limitations of the theory, the agreement is about as good 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.

ELECTROSTATIC MODELS FOR INTERMOLECULAR INTERACTIONS

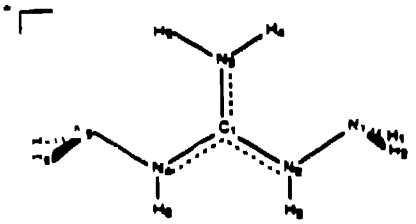
As shown above, we can obtain reasonably accurate predictions for molecules the size of NTO. Another quantity available from these calculations is the total molecular electron density distribution. We believe that this information can be used to approximate the electrostatic component of intermolecular interactions. Since accurate ab initio calculations are still out of reach for systems including two or three or more molecules the size of NTO, we are exploring ways in which the information from a high quality calculation on a single molecule might be used to improve empirical methods for calculating intermolecular interactions among several, possibly up to hundreds, of molecules.

We have previously devised a means of apportioning the total electron density in a molecule among the constituent atoms.[9] The electronic charge distribution associated with an atom in a molecule may then be described by a multipole expansion. Collected together these atom centered multipole expansions (ACME's) describe the total molecular charge distribution in a convenient and compact form. In addition, these ACME's can be used to calculate electrostatic interactions between molecules.[10] Once the ACME's have been obtained, calculation of the electrostatic energy can be done very quickly.[11]

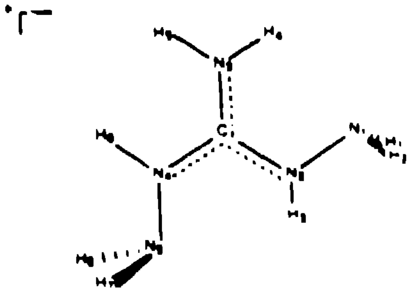
Other workers have shown that electrostatic considerations play a significant role in determining the total energy of intermolecular interactions.[12] This has been especially well studied in hydrogen bonded systems. What is found is that inductive attractions and overlap repulsions nearly balance one another. The electrostatic energy then remains and closely parallels the total energy of interaction.

Despite the recognized importance of electrostatics in determining intermolecular interactions, computer programs used to calculate molecular crystal structures either ignore this effect entirely or include only very rough estimates for it. The techniques we have developed might ultimately be incorporated into crystal structure calculations as a means of using the information available from molecular orbital calculations. Such an approach would provide a means by which the effects of the molecular environment upon a constituent atom might be taken into account.

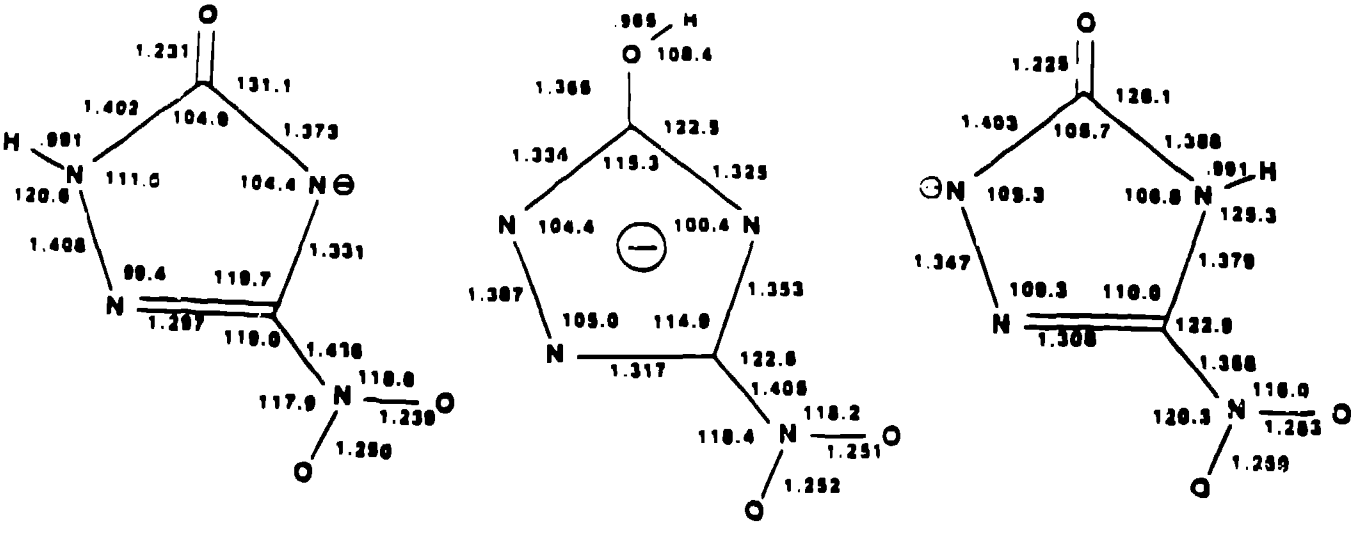
NTO readily reacts with amine bases to produce salts. The diaminoguanidinium salt of NTO has been produced in this fashion at Los Alamos.[13] X-ray structure analysis[14] reveals that the diaminoguanidinium ion of this salt appears in the A configuration indicated below; we denote this geometry as DAGA. Interestingly, X-ray structure analysis of the diaminoguanidinium salt of nitric acid shows another form of the cation,[15] indicated as B, below, which we denote DAGB.



A, C_{2v} Symmetry



B, C_s Symmetry



V VI VII

FIGURE 2. OPTIMIZED GEOMETRIES OBTAINED FROM 3-21G CALCULATIONS

TABLE III. CALCULATED RELATIVE ENERGIES (IN AU) FOR NTO (I) AND ITS CONJUGATE BASES (V-VII) FROM TWO THEORETICAL MODELS.

Model	I	V	VI	VII
3-21G//3-21G	516.17789	515.61923	515.61544	515.60387
6-31G+//3-21G	518.86806	518.33579	518.33510	518.32235

TABLE IV. COMPARISON OF CALCULATED BOND LENGTHS IN V AND THOSE OBSERVED IN THE ETHYLENE DIAMINE SALT OF NTO

Bond	Obs (avg.)	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

The results of molecular orbital calculations for both forms of the diaminoguanidinium ion are summarized in Table V. They show that DAGA, as found in the NTO salt, is higher in energy than DABG, as found in the nitric acid salt. The question to be answered then is why does the conjugate base of NTO selectively bind DAGA when another lower energy form is available?

To answer this question ACME's were obtained for the conjugate base of NTO and both forms of the diaminoguanidinium cation. The electrostatic energy of interaction of the anion with DAGA and DAGB was then calculated for different geometries. The geometries of the anion and cation fragments were fixed at those found in the original MO calculations. Intermolecular distances and angles were varied however to optimize the electrostatic interactions. The complexes were prevented from collapsing by surrounding each atom with a hard sphere, the diameter of which was taken from Bondi.[16]

TABLE V. OPTIMIZED GEOMETRICAL PARAMETERS AND ENERGIES FOR THE A AND B FORMS OF DIAMINOGUANIDIUM ION. SEE TEXT

	A		B	
	3-21G	6-31G*	3-21G	6-31G*
E_{tot}(au)	−312.78369	−314.51739	−312.78526	−314.51830
E_{rel}(kcal)	0.0	0.0	−1.0	−0.6
R(C_1-N_2)	1.304	1.307	1.316	1.317
R(C_1-N_3)	1.334	1.331	1.322	1.321
R(C_1-N_4)	"	"	1.333	1.331
R(N_3-N_5)	1.421	1.386	1.421	1.388
R(N_4-N_6)	"	"	1.422	1.387
R(N_2-H_7)	1.001	0.997	0.998	0.995
R(N_2-H_8)	"	"	1.003	0.998
R(N_3-H_9)	1.000	0.998	1.002	0.999
R(N_4-H_{10})	"	"	1.000	0.998
R(N_5-H_{11})	1.005	1.001	1.006	1.001

Figure 3 shows the minimum energy configurations found for NTO/DAGA and NTO/DAGB. Many other structures were investigated, but these are the lowest energy forms found. The two structures are very similar in their hydrogen-bonding interactions with two N-H moieties of DAG directed toward the carbonyl oxygen and the 4 nitrogen of NTO. These two atoms are the most highly negatively charged of NTO and present the most favorable sites for hydrogen bonding. In both cases, the DAG molecules are skewed toward the oxygen of the nitro group which is also highly negatively charged. Both complexes were found to be planar, although they were not constrained to be so.

The NTO/DAGA complex was found to be 3.4 kcal/mol more stable than the NTO/DAGB complex. The C-$\underline{N}H_2$ nitrogen of DAG is found to be more negatively charged than the C-$\underline{N}$H-NH_2 nitrogens, and should therefore form a weaker hydrogen bond. This appears to be the major reason that DAGA interacts more strongly with NTO than DAGB. A comparison between our calculated structure for the NTO/DAGA complex and the asymmetric unit determined by X-ray crystallography is shown in Figure 4. The electrostatic model is seen to reproduce the observed structure at least qualitatively. Since the difference in energy between the two complexes is larger that the difference in enegy of the isolated molecules, as shown in Table V, it is the electrostatic energy which selectively allows the conjugate base of NTO to bind DAGA.

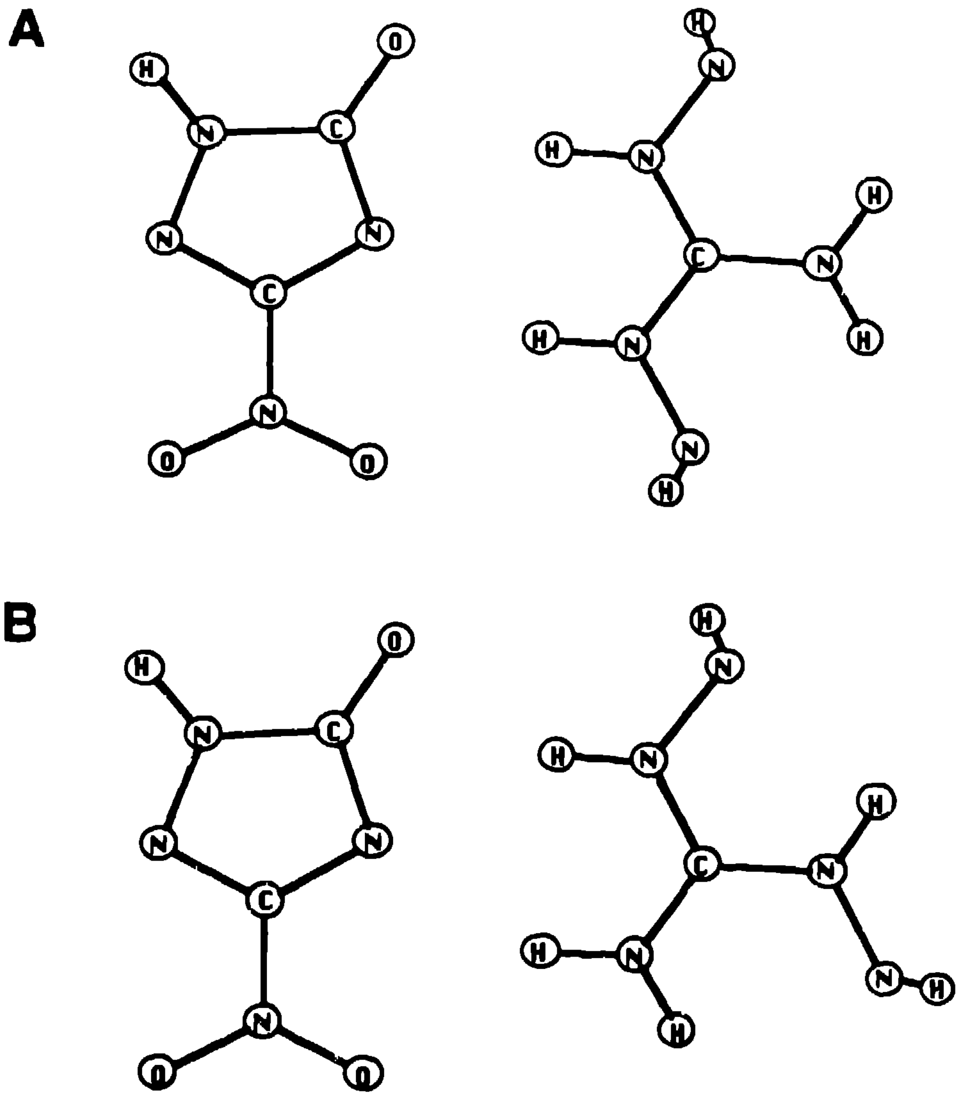


FIGURE 3. LOWEST ELECTROSTATIC ENERGY FORMS FOR NTO/DAGA (A) AND NTO/DAGB (B) ANION-CATION PAIRS.

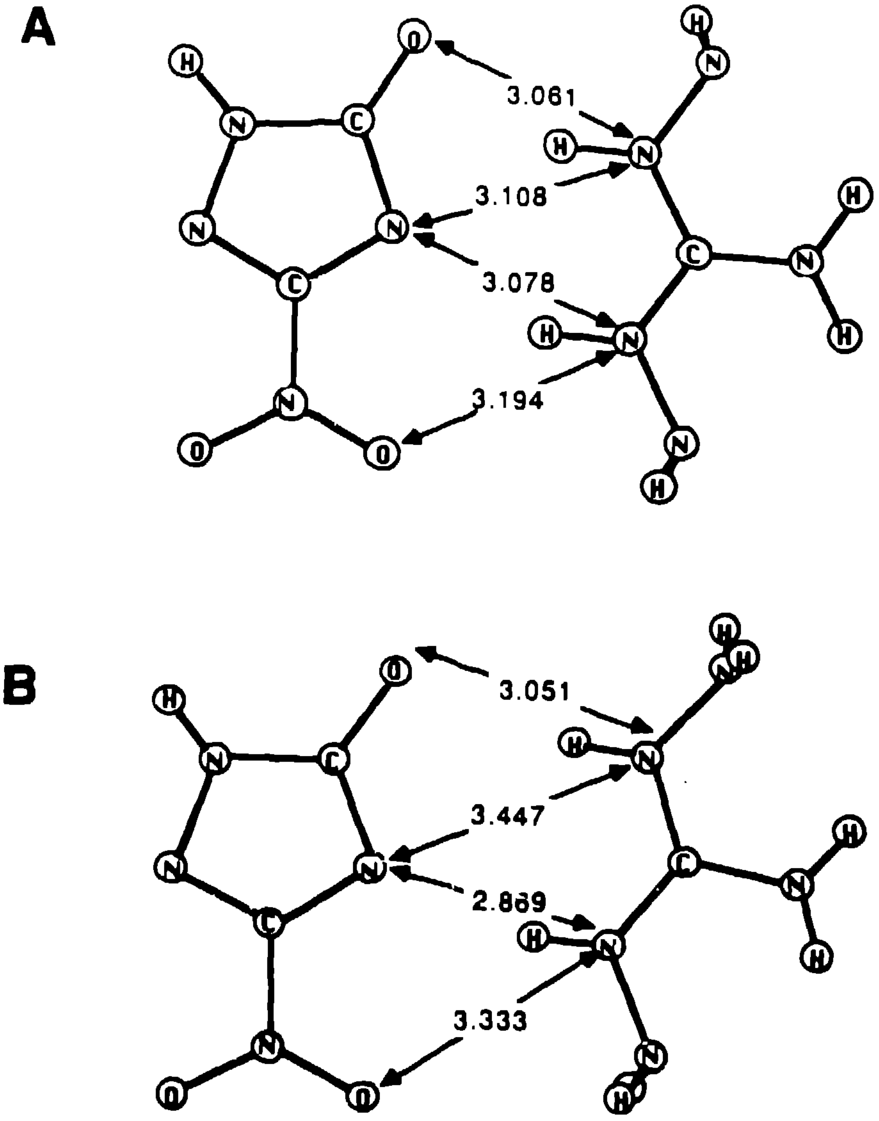


FIGURE 4. COMPARISON OF SOME INTERMOLECULAR DISTANCES FOR THE CALCULATED NTO/DAGA PAIR (A) AND THOSE FOUND EXPERIMENTALLY FOR THE ASYMMETRIC UNIT OF THE DIAMINOGUANIDINIUM SALT OF NTO (B).

CONCLUSIONS

We have demonstrated that MO calculations provide useful information about the structure, energy, and reactivity of NTO. Many of these calculations were performed before the corresponding experiments were performed, indicating that reliable predictions can be made, provided that the molecule is not so large as to preclude the use of large basis sets and other means for performing accurate calculations.

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