Computational Investigation of Amine Complexes of 2,4,6-Trinitrotoluene

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Abstract: Using the B3PW91/6-31G(d) computational procedure, we find two types of complexes to be formed between aliphatic amines and 2,4,6-trinitrotoluene (TNT). Type **1** are noncovalent, primarily electrostatic interactions that occur in the vicinities of the NO_2 groups; Type **2** are σ-adducts, at carbons 1, 3 and 5. In Type **1**, the TNT framework is very little affected. In Type **2**, however, the site of the complex becomes quasi-tetrahedral, with longer bonds to its neighbors in the ring; the $C-NO_2$ bonds are shortened. The Type **1** complexes have weakly negative (attractive) interaction enthalpies. For one of them, utilizing a charge-transfer formalism, we obtained a wave length for an electronic transition to a low-lying dative excited state that is in good agreement with observed values. The Type **2** interaction enthalpies are near-zero or even positive; however all of the complexes correspond to energy minima (no imaginary frequencies). For one of the Type **2**, a transition state to a nitronic acid was found, with an activation enthalpy of only 5.6 kcal/mole. This indicates a possible route for amine-induced decomposition of TNT.

Keywords: trinitrotoluene, amine interactions, hypergolic reactions
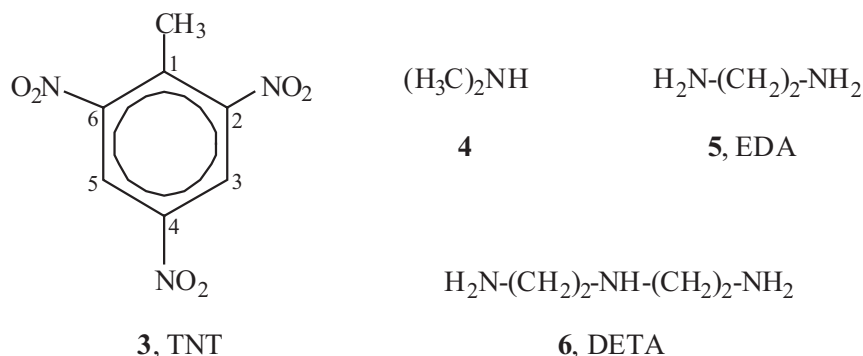
Background and Objectives

The susceptibility of polynitroaromatic molecules to nucleophilic attack is well-established [1-4]. It can readily be understood in terms of the electron-withdrawing power of the nitro groups, which deplete the π charge of the aromatic ring, producing regions of positive electrostatic potential above and below it [5-7], particularly over the C-NO$_2$ bonds. This will be further discussed in relation to Figure 1.

An interesting and important aspect of such reactions in which aliphatic amines are the nucleophiles is that they can lead to the neutralization of nitromaromatic-based explosives, such as 2,4,6-trinitrotoluene (TNT) [8-10], which is a common ingredient of landmines. Introduction of a small amount of an appropriate liquid amine can produce rapid hypergolic ignition and combustion of the nitroaromatic compound without initiating detonation.

The reactions of nitroaromatics with aliphatic amines have long been studied [1-4, 11-20]. A first step appears to often be the formation of a complex. This may simply involve a noncovalent interaction, frequently described as donor-acceptor (or charge transfer) in nature, with the amine serving as the donor; an alternative, or perhaps a second step, may be a Meisenheimer σ-adduct, which is viewed as having a covalent bond (albeit a weak one) between a ring carbon and the amine nitrogen. These two possibilities are shown below for 1,3,5-trinitrobenzene and an amine NR$_3$:

1, noncovalent interaction   **2**, σ-adduct
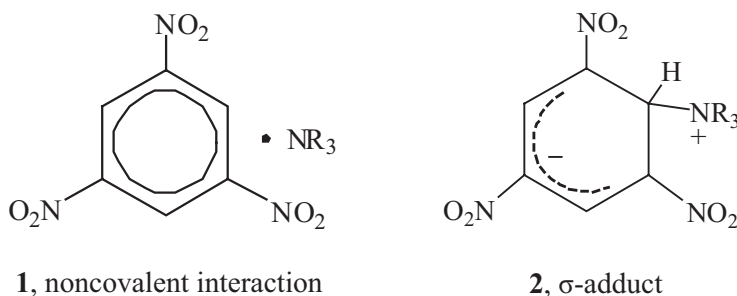
In this work, our objective has been to examine computationally this initial complex formation, using TNT (**3**) as the nitroaromatic molecule. We considered three different amines: dimethylamine (**4**), 1,2-diaminoethane (also called ethylenediamine, EDA, **5**) and 1,5-diamino-3-azapentane (diethylenetriamine, DETA, **6**). The diamine **5** and the triamine **6** can in principle interact through more than one amino group, either with the same or with different TNT molecules.

CH_3 structure:

CH_3 at position 1, O_2N at position 6, NO_2 at position 2, positions 5, 3, 4 with NO_2 at position 4.

$(H_3C)_2NH$

4

$H_2N\text{-}(CH_2)_2\text{-}NH_2$

5, EDA

NO_2

$H_2N\text{-}(CH_2)_2\text{-}NH\text{-}(CH_2)_2\text{-}NH_2$

3, TNT

6, DETA

We found that each of these amines can form complexes of both types **1** and **2** with TNT, depending upon where the interaction takes place. Type **2** was obtained only at carbons 1,3 and 5; type **1** tends to be near the C-NO$_2$ portions of the TNT. It appears that the local reactivity of the TNT molecule plays a determining role, and so we shall begin by examining this, in terms of two key properties: the electrostatic potential and the average local ionization energy.

The Electrostatic Potential

The nuclei and electrons of a molecule create an electrostatic potential V($\mathbf{r}$) in the surrounding space, given by

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \,, \tag{1}$$

where Z_A is the charge on nucleus A, located at $\mathbf{R}_A$, and $\rho(\mathbf{r})$ is the molecule's electronic density. V($\mathbf{r}$) is a physical observable, obtainable experimentally by diffraction methods [21, 22] as well as computationally. It may be positive or negative in any given region, depending upon whether the effects of the nuclei or the electrons are dominant there.

V($\mathbf{r}$) provides an effective means of analyzing noncovalent interactions, which are largely electrostatic in nature [23-25]. For this purpose, we normally compute V($\mathbf{r}$) on the molecule's surface, since this is what is "seen" by another approaching one. We take the surface to be the 0.001 au (electrons/bohr^3) contour of $\rho(\mathbf{r})$, as proposed by Bader *et al.* [26]. This has the advantage of reflecting specific aspects of that molecule, e.g. lone pairs, π electrons, etc. In terms of the features of this surface potential, designated V$_S$($\mathbf{r}$), it has been possible to express

quantitatively a variety of condensed phase physical properties that depend upon noncovalent interactions, such as heats of phase transitions, boiling points and critical constants, solubilities, diffusion coefficients, etc. [23, 25, 27].

For typical organic molecules, the most positive values of $V_S(\mathbf{r})$, the $V_{S,max}$, are associated with hydrogens and sometimes with the σ-holes [28, 29] of covalently-bonded Group IV – VII atoms. Negative regions are often smaller than the positive, but tend to be stronger, with the most negative values, the $V_{S,min}$, being near lone pairs and π electrons. These general patterns can be seen in several compilations [27, 30]. The magnitudes of the $V_{S,max}$ and the $V_{S,min}$ have been shown to correlate with the strengths of both hydrogen bonds [31] and σ-hole interactions [29, 32].

Energetic molecules are, overall, quite different. Positive regions dominate in both strength and extent, a consequence of the strong electron-withdrawing capacities of the nitro groups [5, 6, 30, 33]. Negative $V_S(\mathbf{r})$ are often only on the peripheries of the molecules, by the NO_2 oxygens. The most positive surface potentials, the $V_{S,max}$, are frequently over $C-NO_2$ bonds. This unusual feature, not found for most covalent bonds, has been observed in nitroaromatics, nitroaliphatics and nitroheterocycles. It has been demonstrated that this positive region can serve as a channel for the approach of nucleophiles [7].
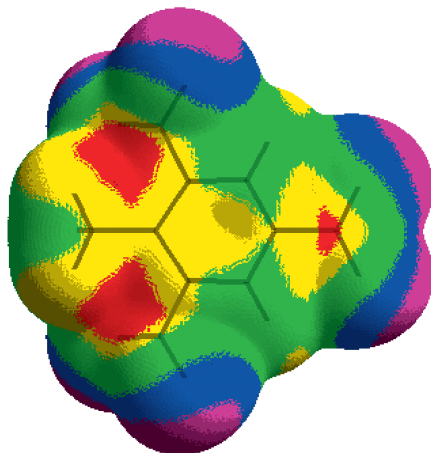
Figure 1. Computed electrostatic potential $V_S(\mathbf{r})$ on the 0.001 au isodensity surface of 2,4,6-trinitrotoluene (TNT, **3**). The methyl group is at the left. Color ranges, in kcal/mole, are: red, more positive than 27; yellow, between 20 and 27; green, between 0 and 20; blue, between -10 and 0; purple, more negative than -10. The most positive (red) regions are over the $C-NO_2$ bonds (near the nitrogens).

In Figure 1 is the electrostatic potential $V_S(\mathbf{r})$ on the 0.001 au surface of the TNT molecule, computed at the density functional B3PW91/6-31G(d) level. The negative potentials above and below the ring that characterize most aromatic molecules, and are due to their π electrons, have been completely eliminated. Most of the surface is strongly positive, with $V_{S,max}$, of 28-35 kcal/mole over the C−NO$_2$ bonds (closer to the nitrogen than to the carbon). As shall be seen, these indicate likely channels for noncovalent electrostatic interactions with nucleophiles.

The Average Local Ionization Energy

While $V_S(\mathbf{r})$ is very useful for interpreting and predicting noncovalent interactions, this is not necessarily the case when there is some significant degree of covalent bonding [34]. For such situations was introduced the average local ionization energy, $\bar{I}(\mathbf{r})$ [35]:

$$\bar{I}(\mathbf{r}) = \frac{\sum_i \rho_i(\mathbf{r})|\varepsilon_i|}{\rho(\mathbf{r})} . \tag{2}$$

In eq. (2), $\rho_i(\mathbf{r})$ is the electronic density of the ith occupied molecular orbital, having energy ε_i.

Within the framework of Hartree-Fock theory, Koopman's theorem [36, 37] provides some support for interpreting $\bar{I}(\mathbf{r})$ as a measure of the energy required to remove an electron from the point $\mathbf{r}$ in the space of a molecule. The focus is upon the point, not upon a particular molecular orbital. The magnitudes obtained for $\bar{I}(\mathbf{r})$ in Kohn-Sham density functional theory differ from the Hartree-Fock, but show the same trends [38, 39] and are equally useful for analyzing the relative reactivities of different sites. For such applications, $\bar{I}(\mathbf{r})$ is usually computed on the 0.001 au molecular surface, and labeled $\bar{I}_S(\mathbf{r})$.

The lowest values of $\bar{I}_S(\mathbf{r})$, the $\bar{I}_{S,min}$, show the locations of the least tightly-bound, most reactive electrons. For example, the $\bar{I}_{S,min}$ of benzene derivatives correctly predict the *ortho*, *para* vs. *meta* directing and ring activating/deactivating effects of different substituents [35, 38]. Experimental pK_a correlate well with the $\bar{I}_{S,min}$ of the corresponding conjugate bases [40, 41]. For an overview of the use of $\bar{I}_S(\mathbf{r})$ in relation to reactive behavior, as well as some fundamental aspects of $\bar{I}(\mathbf{r})$, see Politzer and Murray [42].

Figure 2 presents $\bar{I}_S(\mathbf{r})$ on the 0.001 au surface of TNT, computed with the B3PW91/6-31G(d) procedure. The lowest values associated with the aromatic

ring, the $\bar{I}_{S,min}$, are 11.7 eV, and are located over the carbons bearing NO_2 groups. These would therefore be the least susceptible to nucleophilic attack; the formation of σ-adducts should accordingly be more likely at carbons 1, 3 and 5. This is indeed the case, as shall be seen.
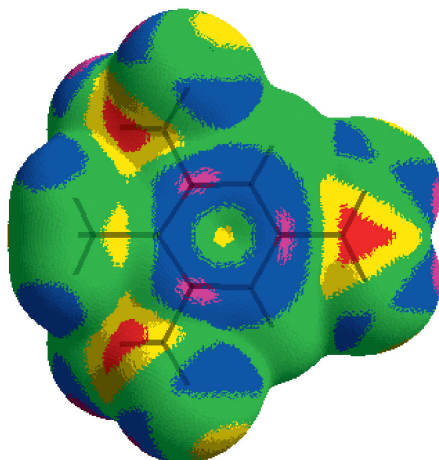

Figure 2. Computed average local ionization energy $\bar{I}_S(\mathbf{r})$ on the 0.001 au isodensity surface of 2,4,6-trinitrotoluene (TNT, **3**). The methyl group is at the left. Color ranges, in eV, are: red, greater than 16.0; yellow, between 14.0 and 16.0; green, between 12.5 and 14.0; blue, between 11.73 and 12.5; purple, less than 11.73. The lowest values (purple) are over the carbons bearing NO_2 groups.

TNT – Amine Complexes

Structures

Each of the three amines (**4**, **5** and **6**) was allowed to interact with TNT at different carbons of the ring. Geometries were optimized, energy minima were verified by the absence of imaginary vibration frequencies, and thermal corrections to 298 K were computed, all at the B3PW91/6-31G(d) level. (A larger basis set was precluded by the sizes of the systems.)

Complexes of both types **1** and **2** were obtained. The type **2**, Meisenheimer σ-adducts, are associated with nucleophilic attack upon a nitroaromatic molecule [1-4], forming a bond with covalent character between a ring carbon and the amine nitrogen (Figure 3). As expected on the basis of Figure 2, this was found to occur only at carbons 1, 3 and 5.
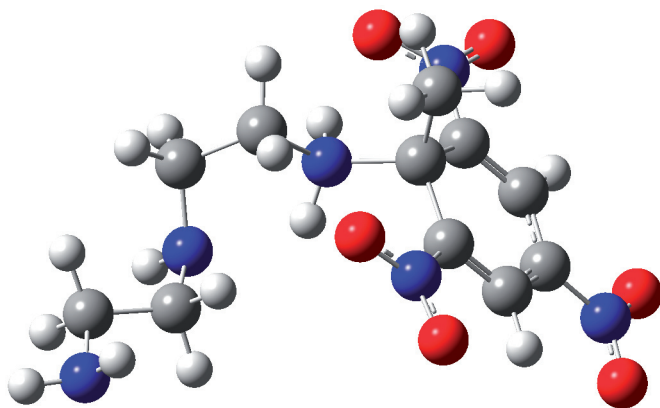
Figure 3. Structure of the Type **2** complex TNT-**6** between TNT and diethylenetriamine (**6**, DETA). The interaction is with C1 of the TNT. (The colors are red for oxygen, blue for nitrogen, gray for carbon and white for hydrogen.)

No σ-adducts were formed at the *ortho* and *para* carbons, which bear NO_2 groups. Instead the amine molecule moved away from the ring, but remained in the neighborhood of the NO_2 group (Figure 4), forming a Type **1** complex in which the amine lone pair appears to be interacting electrostatically with the positive potential over the C-NO_2 bond (shown in Figure 1).
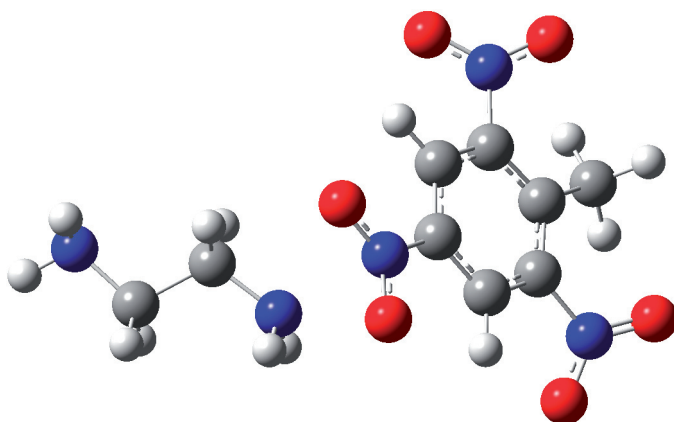
Figure 4. Structure of the Type **1** complex TNT-**5** between TNT and ethylenediamine (**5**, EDA). The interaction is near the para C-NO_2 bond. (The colors are red for oxygen, blue for nitrogen, gray for carbon and white for hydrogen.)

Table 1 compares the computed bond lengths in TNT as a free molecule and in five Type **1** and **2** complexes with the amines **4**, **5** and **6**. There are several points of interest in this table.

Table 1.   Computed bond lengths in TNT and some TNT-amine complexes [a,b]

System:	TNT	TNT-**4**	TNT-**5**	TNT-**4**	TNT-**5**	TNT-**6**
Type of complex:	---	**1**	**1**	**2**	**2**	**2**
Position:	---	*ortho* NO_2	*para* NO_2	C_3	C_1[c]	C_1[c]
Bond lengths (A):						
C_1-C_2	1.409	1.409	1.408	1.401	1.516	1.522
C_2-C_3	1.388	1.387	1.388	1.483	1.373	1.372
C_3-C_4	1.384	1.386	1.383	1.476	1.396	1.396
C_4-C_5	1.384	1.384	1.383	1.369	1.397	1.391
C_5-C_6	1.388	1.389	1.389	1.398	1.372	1.374
C_6-C_1	1.409	1.407	1.408	1.422	1.516	1.529
C_1-C(methyl)	1.503	1.500	1.503	1.506	1.544	1.539
C_2-N(*ortho*)	1.475	1.472	1.474	1.436	1.424	1.433
C_4-N(*para*)	1.470	1.469	1.466	1.425	1.439	1.437
C_6-N(*ortho*)	1.475	1.474	1.474	1.450	1.425	1.426
N_{amine}---$V_{S,max}$[d]	---	1.72	1.22	---	---	---
N_{amine}---C_1	---	---	---	---	1.546	1.574
N_{amine}---C_3	---	---	---	1.638	---	---

[a] Computational level: B3PW91/6-31G(d).
[b] Numbering of carbons given in structure **3**.
[c] The amine nitrogen is slightly closer to C_6 than to C_2.
[d] $V_{S,max}$ over the C-NO_2 bond.

The noncovalent Type **1** interactions have little or no effect upon the bond lengths in TNT. The biggest changes are slight shortenings of the C-CH_3 and C-NO_2 (*ortho*) bonds in TNT-**4** (0.003 Å) and of the C-NO_2 (*para*) bonds in TNT-**5** (0.004 Å). The bond lengths in the amines (not given in Table 1) are also largely unaffected, except for increases of 0.004 and 0.006 Å in the C-N distances in **4**, probably for steric reasons.

Table 1 shows that the interacting amine nitrogens in both TNT-**4** and TNT-**5** are quite close to the $V_{S,max}$ over the nearest C-NO_2 bond; the $N_{amine} - V_{S,max}$ separations are about 1.72 and 1.22 Å, respectively. Since the van der Waals radius of nitrogen is 1.55 Å [43], it seems justified to conclude that the nitrogen lone pair is interacting with the positive channel represented by the C-NO_2 $V_{S,max}$, as suggested earlier.

In contrast to the Type **1** complexes, the Type **2** show marked changes in the TNT framework. The carbons at which the interactions occur become quasi-tetrahedral, and their bond lengths to the neighboring ring carbons increase from the aromatic 1.38-1.41 Å to 1.48-1.53 Å. The other C-C distances around the ring are, for the most part, in the 1.37-1.40 Å range.

The C-NO$_2$ bonds in the Type **2** systems are significantly shorter than in TNT, by 0.03-0.05 Å. This seems to be the result of the ring having gained some electronic charge density, from the amine lone pair; we have seen the same effect in the negative ion of TNT, TNT$^-$ [44], and there are even indications of it in the noncovalent Type **1** complexes in Table 1. These observations are consistent with the fact that the depletion of charge density in the ring in going from mono- to trinitrobenzene progressively lengthens and weakens the C-NO$_2$ bonds [45].

The N$_{amine}$-C$_1$ and N$_{amine}$-C$_3$ distances in the Type **2** complexes, while longer than the 1.45-1.47 Å that is more typical of a C-N single bond, do indicate the covalent character of the interaction. The C-N bond to this nitrogen within the amine molecule is 0.03-0.04 A longer than in the free amine.

A final point of interest, the importance of which will become evident later, is that there is evidence of N-H---O-N interactions involving the amines and the nearest nitro groups in the Type **2** complexes. The respective N-H and O-N bond lengths increase by about 0.04 Å and 0.02 Å, and the H---O separations are 1.8-1.9 Å, well below the sum of the van der Waals radii, 2.7 Å [43].

Energetics

Table 2 lists the computed interaction enthalpies at 298 K for the formation of a group of Type **1** and **2** complexes. These are defined as,

$$\Delta H = H_{complex} - [H_{TNT} + H_{amine}] \tag{3}$$

Given the relatively small basis set used for these calculations, 6-31G(d), which was necessitated by the sizes of the systems, the data in Table 2 should be viewed as indicative rather than definitive.

The ΔH(298 K) for the Type **1** complexes show attractive but weak interactions. The fact that they are slightly stronger at the *ortho* NO$_2$ is consistent with the V$_{S,max}$ over the *ortho* C-NO$_2$ bonds being more positive (35 kcal/mole) than that over the *para* (29 kcal/mole).

Table 2. Computed interaction enthalpies for formation of TNT-amine complexes, TNT + amine → complex [a,b]

Complex	Type	Position	ΔH(298 K), kcal/mole
TNT-**4**	1	*ortho* NO_2	-3.0
TNT-**5**	1	*ortho* NO_2	-2.7
TNT-**5**	1	*para* NO_2	-0.8
TNT-**4**	2	C_3	6.9
TNT-**5**	2	C_1	-0.6
TNT-**5**	2	C_3	0.1
TNT-**6**[c]	2	C_1	5.2
TNT-**6**[c]	2	C_3	0.8
TNT-**6**[d]	2	C_3	-0.3

[a] Computational level: B3PW91/6-31G(d).
[b] Numbering of carbons given in structure **3**.
[c] Terminal nitrogen in **6**.
[d] Middle nitrogen in **6**.

The Type **1** interactions are often labeled donor-acceptor or charge-transfer. These terms actually describe the characteristic electronic transition to a low-lying dative excited state, rather than the interaction in the ground state. We examined this feature in the case of TNT-**4**, using the formalism of Flurry and Politzer [46], according to which the transition energy ΔE_{CT} is given approximately by,

$$\Delta E_{CT} = I - A + V_{es} - 2\Delta E \tag{4}$$

In eq. (4), I is the ionization energy of the electron donor, $(H_3C)_2NH$; A is the electron affinity of the acceptor, TNT, and V_{es} represents the electrostatic interaction energy between TNT^- and $(H_3C)_2NH^+$. ΔE is the energy of interaction between TNT and **4**, obtained by the analogue of eq. (3), which we found to be -3.6 kcal/mole $= -0.16$ eV. For **4**, I = 8.24 eV [47]. We were unable to find an experimental A for TNT, so we computed it at a high level, B3PW91/6-311++G(3d,2p), which yielded A = 2.43 eV. V_{es} was determined by the procedure of Ma and Politzer [48]; $V_{es} = -58.5$ kcal/mole $= -2.54$ eV. Insertion of these values into eq. (4) leads to $\Delta E_{CT} = 3.59$ eV, which corresponds to a wavelength of 346 nm for the electronic transition. This is in exactly the spectral region in which have been observed absorption bands that were attributed to charge-transfer complexes between nitroaromatics and aliphatic amines [11, 14, 17].

The Type **2** systems in Table 2 all correspond to energy minima; however the interaction enthalpies are near-zero or even positive. In one case, TNT-**5** at C_3, we

looked for and located the transition state for the formation of this complex. The N_{amine}-C_3 distance in the transition state is 1.975 Å, and the activation enthalpy is 3.8 kcal/mole.

We also investigated the possibility of **5** or **6** forming a double Type **2** σ-adduct with a TNT molecule, interacting simultaneously through two amine groups at different carbons. We did find one example of this, a Type **2** TNT-**5** complex involving C_3 and C_5 of TNT. However the enthalpy of interaction, $\Delta H(298\ K)$, is 21.8 kcal/mole.

Discussion and Summary

As was pointed out by Buncel [3], the formation of Type **1** and Type **2** complexes (the focus of the present work) are two of several possible initial steps in the reactions of amines with TNT. Others include electron transfer from the amine to produce TNT^- and proton transfer from either the methyl group or C_3 of TNT to the amine. In the gas phase, these latter processes would require large inputs of energy. The ionization energies of **4**, **5** and **6** are in the general neighborhood of 8.5 eV [47]. Using A = 2.43 eV for TNT (see above), ΔE for electron transfer would be about 6.1 eV or 140 kcal/mole. For proton transfer from the methyl group of TNT to **4**, **5** and **6**, our calculated $\Delta H(298\ K)$ are between 80 and 104 kcal/mole. The energetics of these processes might of course be significantly more favorable in an appropriate solvent. Thus a TNT-amine reaction may have one or more initiating steps, perhaps simultaneously, depending upon the circumstances. However the occurrence and importance of Type **1** and Type **2** complexes between nitroaromatics and amines is well established [1-4, 11-20].

Additional supporting evidence is provided by calculated and experimental vibration frequencies. We computed these for TNT itself and for three Type **2** complexes: TNT-**5** (C_1), TNT-**6** (C_1) and TNT-**6** (C_3). Of particular interest is a TNT mode that we found at 963 cm^{-1}, consisting primarily of stretching the C-NO$_2$ bonds. This is not present in the three complexes. However the latter have similar modes in the 974-980 cm^{-1} range (which were not obtained for TNT). What is significant, that when TNT was reacted with several different amines, including **6**, a color change to dark red was observed in each case and an infrared band appeared at around 980 cm^{-1} [49].

Assuming that a Type **1** or Type **2** complex has been obtained in an early stage of a TNT-amine reaction, what might happen next? This will be the subject of future studies. However we already have an indication of one possibility:

we found a transition state for the conversion of Type **2** TNT-**4** to a nitronic acid, via the migration of the amino hydrogen to an oxygen of the neighboring *para* NO_2; the shortness of the NH---ON separations in the Type **2** systems was already pointed out. This results in the *aci* tautomer of the complex, which is a nitronic acid. The transition state is shown in Figure 5; it has one imaginary frequency, corresponding exactly to the movement of the hydrogen between the amino nitrogen and the nitro oxygen. Its distances from these atoms are 1.468 and 1.095 A, respectively. The activation enthalpy $\Delta H_{act}(298$ K) is just 5.6 kcal/mole. Nitronic acids are often quite unstable [50], and they have been proposed as possible intermediates in the decomposition processes of some energetic compounds [51, 52]. Thus the seemingly facile *aci* tautomerization of the Type **2** complex TNT-**4** suggests a possible mechanism for the amine-induced decomposition of TNT.
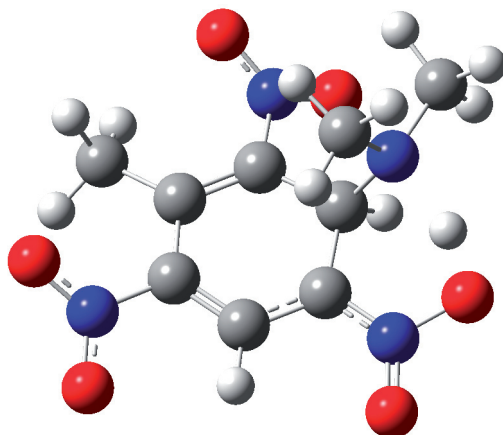
Figure 5. Structure of the transition state for the conversion of the Type **2** TNT-**4** complex between TNT and dimethylamine (**4**) to the nitronic acid *aci* tautomer. (The colors are red for oxygen, blue for nitrogen, gray for carbon and white for hydrogen. The migrating hydrogen is at the right, in the middle.)

In this context, it is relevant to mention the experimental studies of Tulis *et al*. [8], who measured the time delay to the hypergolic ignition of TNT by several compounds, including **5** and another amine, pyrrolidine, at different temperatures. They found Arrhenius-like correlations between the time delays and the reciprocals of the Kelvin temperatures. If we assume that the time required for ignition is inversely proportional to the activation energy ΔE_{act}, then we can

use their results and the Arrhenius equation to make rough estimates of ΔE_{act}. We obtain $\Delta E_{act} = 5$–6 kcal/mole for **5** and $\Delta E_{act} = 6$–7 kcal/mole for pyrrolidine, as the approximate activation energies for the hypergolic ignition of TNT by these two amines.

It is fortuitous that these activation barriers estimated from experimental data are so close to that computed for the *aci* tautomerization of the Type **2** TNT-**4** complex. But the fact that they are at least similar and also very small indicates that the involvement of *aci* tautomers of Type **2** complexes in the hypergolic ignition of TNT by amines merits consideration.

Acknowledgement

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