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A QUANTUM MECHANICAL STUDY OF
THE INITIAL DECOMPOSITION OF RDX

by
Mehmet Ali Baran

A Thesis
Presented to the Graduate Committee
of Lehigh University
in Candidacy for the Degree of
Master of Science
in
Mechanical Engineering

Lehigh University

1981

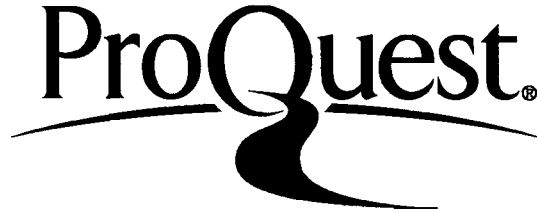
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A QUANTUM MECHANICAL STUDY OF THE INITIAL
DECOMPOSITION OF RDX

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ABSTRACT

RDX is the code designation of the compound cyclo-trimethylene-trinitramine, $C_3H_6N_6O_6$, which is a well known explosive. It is also known as cyclonite and has a melting point of $205^{\circ}C$. An orthorhombic symmetry is possessed by RDX, the plane defined by the three carbon atoms and the plane of approximate mirror symmetry being perpendicular to each other. The most probable space group is P_{bca} and the unit cell of this compound contains eight molecules. Available literature provides the reaction mechanisms and the coordinates

of the equivalent positions of eight molecules in the unit cell.

There are several quantum mechanical computational techniques among which Consistent Force Field Method has an important place. The difficulty of applying this method to RDX is that the previous developments does not involve nitrogen compounds. Warshel and Levitt have written a program (QCFF/PI) which is a quantum mechanical extension of consistent force field to pi electron systems. If the atomic potential parameters are available QCFF/PI program can calculate equilibrium configuration and vibrational normal modes of ground and pi excited states of large conjugated molecules and of the ground state of any other molecule.

The first aim of the present study is to extend Consistent Force Field Method to include molecules involving nitrogen such as RDX. The second aim is to examine the breakdown of RDX when activated by an external source. To do this a chemical path is chosen among the available reaction mechanisms. Finally, the chemical decomposition mechanism is combined with the modified Consistent Force Field Method and estimates of the likelihood of the events made based on the molecular energy.

As a result of first calculations, the heat of formation of RDX was found to be 390.53 kcal/gmole. It is concluded

that the initial breakup of this molecule would require the removal of an NO_2 group. There were two possibilities for the separation of NO_2 group. One of the possibilities was the movement of nitrogen atom between the two oxygen atoms and the second possibility involved the movement of NO_2 group as a whole. Both possibilities were investigated during this study and it was seen that the amount of energy required to separate NO_2 group as a whole (64.47 kcal/gmole) is more than the energy required to move the nitrogen away between the two oxygen atoms (58.99 kcal/gmole). The conclusion as a result of these figures, was that the separation of NO_2 can be achieved by moving the nitrogen atom between the two oxygen atoms and not by moving the NO_2 group as a whole.

The numerical results of this work are obtained by using the CDC computer system of Lehigh University.

CHAPTER I
INTRODUCTION

Conjugated molecules containing nitrogen and oxygen heteroatoms play an important role in the area of biological processes and explosives. The field of interest of this study is one of the most powerful explosives known at the present time, namely, RDX.

Many professionals tend to review the subject of explosives from a purely military standpoint. Explosives are among the most powerful servants of man. Large engineering projects like tunnels or dams would have taken hundreds of years if performed by hand and labor only. Mining of all kinds depends on blasting, as does cleaning of stumps and large boulders from land. Recent use of controlled underwater explosives to shape metals offers a steadily growing outlet and presents a new, and economical method for fabricated techniques.

An explosive is a material which under the influence of thermal or mechanical shock, decomposes rapidly and spontaneously with the evolution of a great deal of heat and much gas. Only those of being controlled and having a high

energy content are of importance commercially or in a military sense.

RDX is among the military explosives and is used in a mixture with TNT and aluminum known as Torpex, for mines, depth charges and torpedo warheads. It is also employed as an ingredient for explosives, for shells and bombs and it is desensitized by wax or oily materials.

It is very important and necessary to understand the reaction mechanisms of explosives. Semi empirical methods are used for such studies. The total energy of a molecule can be calculated by using such methods for a given configuration. It is also possible to find the minimum potential energy surfaces around the molecule if the original configuration is deformed in various directions. One of the available quantum mechanical computational methods is Consistent Force Field Method. In this approach the empirical potential is determined by choosing parameters and functional forms such that the calculated values of molecular properties depending on the zeroth, first and second derivatives of the Taylor's expansion agree in a least squares sense with the corresponding experimental results. The method has been used previously for alkanes, and in a somewhat approximate form, for other molecules that can be described in terms of localized bonds. The aim of this work is to apply this method- Consistent Force Field Method¹- to RDX molecule which is a complex con-

jugated molecule containing nitrogen and oxygen heteroatoms. The primary objective of using such techniques is to obtain accurate and reliable molecular properties in particular areas of chemistry where experimental data are lacking or where current experimental procedures fail. It is necessary to keep the cost of calculations within bounds while developing and using such methods.

In the present approach a new configuration is sought each time the potential energy of the proposed configuration exceeded the activation energy. It must be noted that it is questionable whether the results will be meaningful or not since the other members of the crystal lattice are not considered by the potential surface.

In this manuscript, chapter II is used to describe the chemistry of RDX both below and above its melting point. The reaction mechanisms available in the literature are listed and a chemical path is chosen from available literature. Also, the properties and coordinates of equivalent positions of RDX molecules in the unit cell are given in this chapter.

Consistent Force Field Method is described briefly in the beginning of chapter III. The program developed by Warshel and Levitt² can be used for conjugated hydrocarbons without any difficulty. The problem of applying this method to RDX is that it has not been previously used with nitrogen compounds. Therefore, several problems were encountered with the use of

Warshel and Levitt program which required the modification of the available program. Lappicirella and Warshel³ discussed the possibilities of extending QCFF/PI program to heteroatom conjugated molecules. Under the light of their approach some modifications and changes were done in the available program. The basis of these modifications are also discussed in this chapter. Then the basic ideas behind using a chemical formula to express the connectivity of RDX molecule are listed.

Finally, chapter IV serves to summarize and discuss the results obtained from combining the chemical decomposition mechanism of chapter II with the Consistent Force Field Method presented in chapter III.

CHAPTER II
CHEMISTRY OF RDX

The compound cyclotrimethylene-trinitramine, $C_3H_6N_6O_6$, also known as cyclonite, or by the code designation RDX, is a well known explosive. The molecule consists of alternate CH_2 and $N-NO_2$ groups in a puckered ring. The environment of the carbon atoms are essentially tetrahedral; and the $N-NO_2$ groups are planar. The molecule possesses a plane of approximate mirror symmetry perpendicular to the plane defined by three carbon atoms. The melting point of the molecule is $205^\circ C$. The compound crystallizes in the orthorhombic space group P_{bca} with the unit cell dimensions $a = 13.182 \text{ \AA}$; $b = 11.574 \text{ \AA}$; $c = 10.709 \text{ \AA}$. The unit cell contains eight molecules, Choi and Prince⁴.

The coordinates of equivalent positions of the eight molecules in the unit cell are given by:

$$\begin{array}{ll}
x, y, z; & \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \\
\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; & \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \\
\bar{x}, \bar{y}, \bar{z}; & \frac{1}{2} - x, \frac{1}{2} + y, z; \\
x, \frac{1}{2} - y, \frac{1}{2} + z; & \frac{1}{2} + x, y, \frac{1}{2} - z.
\end{array}$$

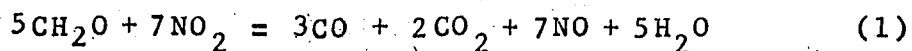
Choi and Prince⁴ provides the general x,y,z coordinates of an RDX molecule. The locations of the other seven molecules forming the unit cell are calculated using the above information available for P_{bca} space group.

Thermal Decomposition of RDX Below Its Melting Point

Cosgrove and Owen^{5,6} obtained the pressure-time curve for the thermal decomposition of RDX below its melting point. The results have been interpreted as a slow solid reaction leading to a product which liquifies the reactant at the temperature of the experiment and accelerates its decomposition. The ratio of the rates of the decomposition in the liquid and solid phases is said to be approximately 10:1. The decomposition has been studied and it has been concluded that the initial reaction occurs in the gas phase and not in the solid state. It was further concluded that at 195°C RDX does not decompose

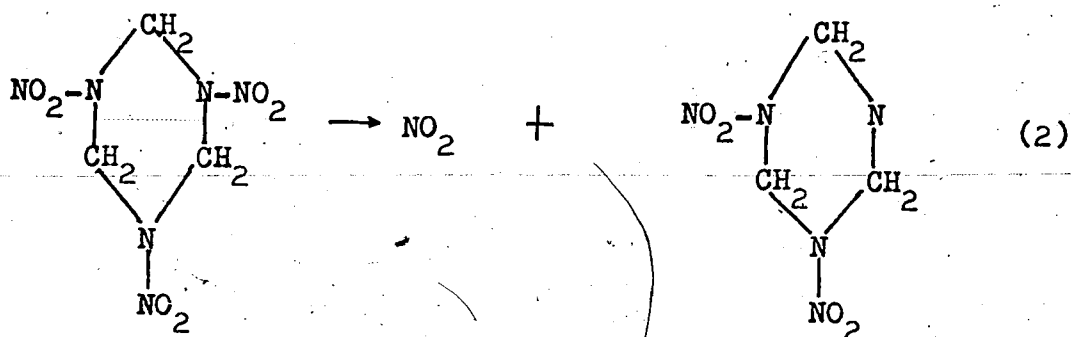
in the solid state to any significant extent. Finally, the rate of reaction in the gas phase is at least equal to that in the liquid phase.

Hydroxymethyl formamide and polymeric materials formed from hydroxymethyl formamide have been shown to be the major products. These comparatively low molecular weight materials are highly hydrogen bonded liquids of low volatility which subsequently act as a solvent for RDX. Nitrogen, due to its effect on the rate of diffusion of RDX vapor away from the crystal surface, is shown to have an inhibiting effect. At 195°C the products of decomposition which were isolated and identified were nitrogen, nitric oxide, nitrous oxide, carbon dioxide, carbon monoxide, water, methylol formamide, and similar compounds formaldehyde, hydrogen cyanide, a nitrate and a nitrile. At this temperature formaldehyde reacts vigorously with NO₂;

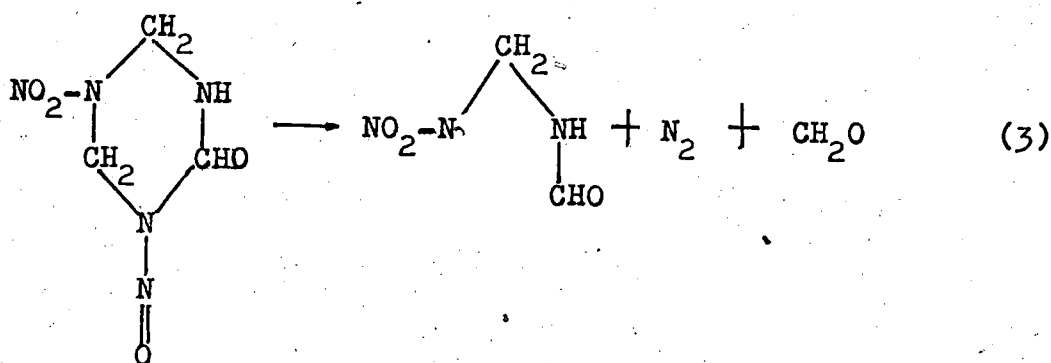


At 195°C different initial steps in the mechanisms are indicated for the gaseous and solution phase decompositions. The first step in the decomposition of RDX in the gaseous phase is the elimination

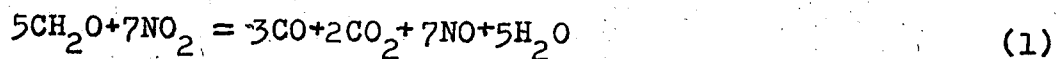
of nitrogen dioxide.



The radicle then breaks down possibly according to the scheme given below:



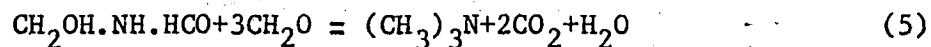
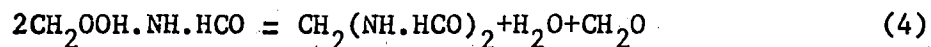
Nitrogen dioxide and formaldehyde react rapidly at 195°C; the reaction being first order with respect to each reactant. This reaction is represented by :



It is suggested that the .CHOH.NH.CHO. radical would be stabilized by delocalization of electrons and hydrogen bonding. Subsequent reaction with a proton

would lead to hydroxymethyl formamide or alternatively the radical could dimerise.

Hydroxymethyl formamide decomposes slowly at reaction temperature to give methylene diformamide, CO_2 , formaldehyde, trimethylamine, and water according to the equations:



It is possible that the amine nitrate observed in the decomposition of RDX is trimethylamine nitrate. The pyrolysis of hydroxymethylformamide is retarded the presence of nitric acid. Under acid conditions, there is a greater tendency for the formation of a liquid product which is believed to be a polymer of hydroxymethyl formamide e.g.



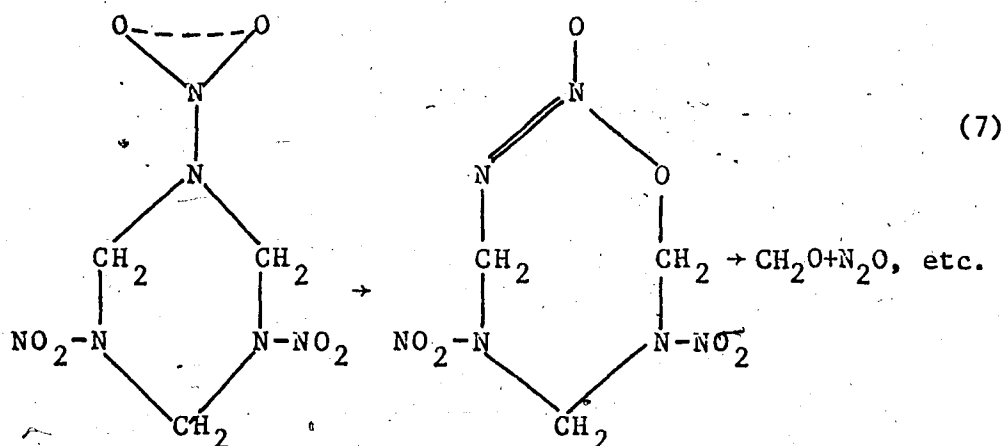
The activation energy for the separation of the NO_2 group was found to be 48.7 kcal/kgmole.

It will be assumed for the present purposes that once the ring is broken, then the remaining

steps in the reaction will occur very rapidly.

Thermal Decomposition of RDX Above the Melting Point

The earliest work done was the study of Robertson⁷. It was suggested that the primary step involved is the transfer of an oxygen atom from the nitroamino group to a neighboring carbon followed by the elimination of CH_2 and N_2O , possibly through an oxadiazole intermediate.

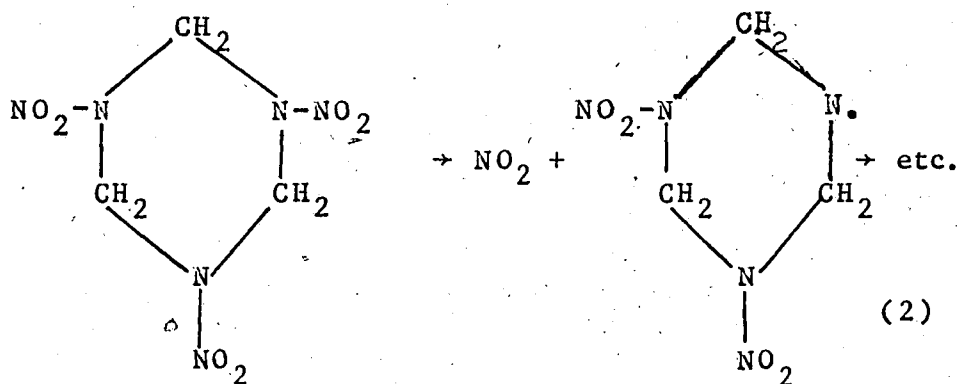


Activation energy = 47.5 kcal/kgmole.

Later on Ranch and Fanelli⁸ concluded that at temperatures above the melting point decomposition occurs simultaneously in the gas phase and in the liquid phase, and further that the mechanism of the gas phase decomposition is not the same as that for liquid, the former almost certainly, involving

rupture of the nitroamine N-N bond, and formation of NO_2 , whereas the latter does not.

The rapid initial production of NO_2 suggests that the first step in the gas phase decomposition mechanism is the homolytic rupture of the nitroamine N-N bond in a unimolecular process.



It is interesting to note, however, that with small enough initial weights and very large reactors, it should be possible, in principle, to isolate the gas phase decomposition. The gas phase decomposition makes a negligible contribution to the overall rate under most condition.

CHAPTER III
A QUANTUM MECHANICAL COMPUTATIONAL METHOD
CONSISTENT FORCE FIELD METHOD

This method had not been previously developed sufficiently for use with nitrogen compounds. The major advantage with this approach is that the calculations do not require either as much time or computer storage per molecule as Molecular Orbital techniques. Thus it was possible to undertake an extensive analysis with this system.

The program Warshell and Levitt² (QCFF/PI) is a quantum mechanical extension of the consistent force field to pi electron systems which calculates equilibrium configurations and vibrational normal modes of ground and pi excited states of large conjugated molecules as well as of the ground state of any other molecule for which the potential parameters are available.

This method is based on a formal separation of sigma and pi electrons with the former represented by analytical representation of semi-empirical model of the Pariser-Parr-Pople type (corrected for orbital overlap).

The potential surfaces are provided in terms of $3n$ cartesian coordinates of the molecule used. $3n$ coordinates are chosen as the basis set of independent coordinates to treat all possible molecular degrees of freedom in an efficient way. In the cartesian space the kinetic energy matrix is diagonal and the potential energy is defined even for cyclic molecules, without the use of redundant conditions. This helps when dealing with cyclic molecules such as RDX. Also, the complete set of analytical second derivatives of the potential with respect to cartesian coordinates can be evaluated efficiently for any molecule and any potential. But, for example, to evaluate the second derivatives with respect to $3n-6$ independent internal coordinates for cyclic molecules is almost impossible. The availability of the cartesian second derivative matrix and the diagonal nature of the kinetic energy matrix allows for a straight forward normal mode

analysis for any type of potential.

The pi integrals for hydrocarbons and the Consistent Force Field (CFF) parameters of the potential functions are included in the program. An approximation can be used to get the set of parameters for other molecules. The potential surface and its first and second derivatives with respect to the cartesian coordinates are given in an analytical form. The molecular energy is minimized efficiently by the modified Newton-Raphson method and by evaluation of the vibrational frequencies by diagonalization of the matrix of mass scaled second derivative.

An essential element in the effectiveness of the procedure is the availability of analytical expressions for the potential energy and the required derivatives. The sigma-electron energy and its derivatives can be evaluated directly at each point in the coordinate space without the excessive use of computer time. However, the pi-electron energy was estimated by a more simplified procedure. For the steepest descent method employed in the initial stages of finding the minimum energy configuration, the first derivatives of the potential energy are

required. The bond orders are calculated at the beginning of each step and then change in energy is determined as a function of coordinates. For the modified Newton-Raphson method the second derivatives of the potential energy with respect to the system coordinates must be obtained. During these iteration procedures the cartesian coordinates of the molecule are changed, and the new coordinates are used in calculations. However, the final results show that, for RDX, the coordinates after the relaxation of the molecule differ on the average by 0.1 of an angstrom, with a maximum of 0.419, from the initial coordinates of the molecule. The potential parameters and the parameters in the pi integrals used in this program must be provided as input.

This method has been developed and used successfully for conjugated hydrocarbons. It has not previously been used with nitrogen compounds. Considerable progress has been made by Lapricirella and Warshel³ to extend this method to heteroatom conjugated molecules. The basic problem with conjugated molecules containing oxygen and nitrogen heteroatoms is that the sigma electrons may be strongly polarized and this will alter corresponding

pi-electron core potentials. Thus the sigma-electron core is no longer constant and the changes of the sigma charges strongly change the local potentials of the pi-electrons. In order to retain the advantages of QCFF/PI approximation the sigma-pi separability approach must be formulated. This formulation has been studied by Lappricirella and Warshell³, where the pi-electron treatment is reformulated. The interaction with the sigma-electrons is incorporated while retaining the sigma-pi separability assumption. It is necessary to undertake some modifications basically in the diagonal elements of the Fock matrix F, while the off-diagonal elements of this matrix remain unchanged. Also in the original discussions the elements of the core hamiltonian matrix H, are defined as:

$$H_{ii} = W^0, \quad i = 1, 2, \dots, 6 \quad (8)$$

where 6 is the number of pi atoms for RDX molecule, and these pi atoms are pyridine type nitrogens. They are referred to as M throughout this study. W^0 's are one of the empirical constants for alpha integrals and they are available in the input of the program for every pi atom. Alpha integrals are among the potential functions.

The above equation (8) is modified to:

$$H_{ii} = W^0 + Q_M^\sigma \gamma_{MM} \quad (9)$$

In equation (9) Q_M^σ is the net sigma charge on the pi atom and is assumed to be constant.

$$Q_M^\sigma = -0.21 \quad (10)$$

γ_{MM} is the empirical analytical gamma function. Constants for this function are defined in input of the program.

The modifications on the diagonal elements of the core Hamiltonian matrix H, are made for pi atoms only.

Another modification is made by changing Z to

$$Z = Z + Q_M^\sigma \quad (11)$$

where the original values of Z are defined in the original program.

Normally, separated-atom configuration of the pyridine type nitrogen is given by the following equation:

$$1s^2 \ 2s^2 \ 2p_\sigma^2 \ 2p_\pi^1 \quad (12)$$

But, actually in a molecule, the charge distribution of pyridine type nitrogen is given by Clementi⁹ as follows:

$$1s^2 \quad 2s^{1.51} \quad 2p_{\sigma}^{2.70} \quad 2p_{\pi}^{1.01} \quad (13)$$

As a result of this configuration the pyridine type nitrogen is negatively charged by 0.22 electrons. In other words, the net charge on nitrogen atom is -0.22. Each nitrogen in the molecule has gained 0.22 of an electron. This gain is the sum of two effects: a gain of 0.21 of an electron from the sigma Orbital and a gain of 0.01 of an electron from the pi-Orbital. The nitrogen atom acts as a sigma and pi acceptor with the net result of a gain of 0.22 of an electron. This value may differ slightly for each nitrogen atom in the molecule, but in this study it is assumed that every nitrogen is charged negatively by 0.22 electrons. Similarly, every carbon atom in the molecule is assumed to be negatively charged by -0.25 electrons, and oxygens are assumed to be positively charged by 0.25 electrons. This kind of procedure ends up with a total charge of -0.57 electrons on the molecule. In order to equate the total charge on the molecule to zero, using the discussions, in^{10,11}, it is assumed that the excess charge is obtained equally by 6

hydrogen atoms in the molecule. Therefore, each hydrogen atom is positively charged by 0.095 electrons. The hydrogens and oxygens are sigma donors, while the carbon atoms are sigma accepters. In the original program the net charges on atoms are chosen to be zero. For the case of RDX molecule the atomic charges of carbon, nitrogen, hydrogen, and oxygen atoms are modified to be -0.25, -0.22, +0.095, +0.25 respectively using the discussions by Clementi. Finally, a refined set of data for constants used to evaluate the empirical analytical integrals including the data for atoms such as nitrogen and oxygen are given by Lappicirella and Warshel³. These data are used wherever applicable. For the cases where the nitrogen bond characteristics are still unknown, the carbon bond strengths are used as an approximation. However it is believed that the error for these approximations may only be a factor of 2 or 3 in the absolute values and the relative changes with bond stretching may be less.

The hydrocarbon parameters are contained within the program. The corresponding atomic codes are C for Sp^3 (CH_2) carbon, B for Sp^3 methyl carbon, H, for hydrogen, (D for Deutrium), and A for Sp^2

carbon atom. The codes O, N and M are reserved for ketone oxygen, for pyrrole nitrogen and for pyridine nitrogen (all these are pi atoms). All other codes (Q,R,T,X,Y,Z,W) can be used for any other atom.

In case of RDX molecule, the carbon atoms form CH_2 groups. In other words they are Sp^3 carbons and the corresponding atomic code is C. The oxygens are given the code Q arbitrarily, since they are not ketone oxygen. Finally pyridine type nitrogens are coded by the letter M. The ring nitrogens are labelled M_{1-3} and the nitrogens in the NO_2 groups are M_{4-6} . Oxygen atoms Q_{1-2} are associated with M_4 , Q_{3-4} with M_5 etc.

One of the important steps in running the program is using a chemical formula to express the connectivity of the molecule. As explained above the atoms are represented by the letters (HONCABDM, QRTXYZW). The connectivity is defined by the order of the atomic symbols and a few special symbols. The atoms in the molecule are classified in two groups as "side atoms" and "chain atoms". Side atoms are connected to only one atom in the molecule, while the chain atoms can have connections with more than one atom. For the case of RDX molecule hydrogens are

connected to carbons, and the oxygens are connected to nitrogens only, hence H and Q are side atoms (Figure 1).

The symbolic notation can be used most efficiently by following steps:

(a) The molecule is drawn in two dimensions (Figure 1) using the appropriate symbols for atoms and connecting the bonded atoms with straight lines.

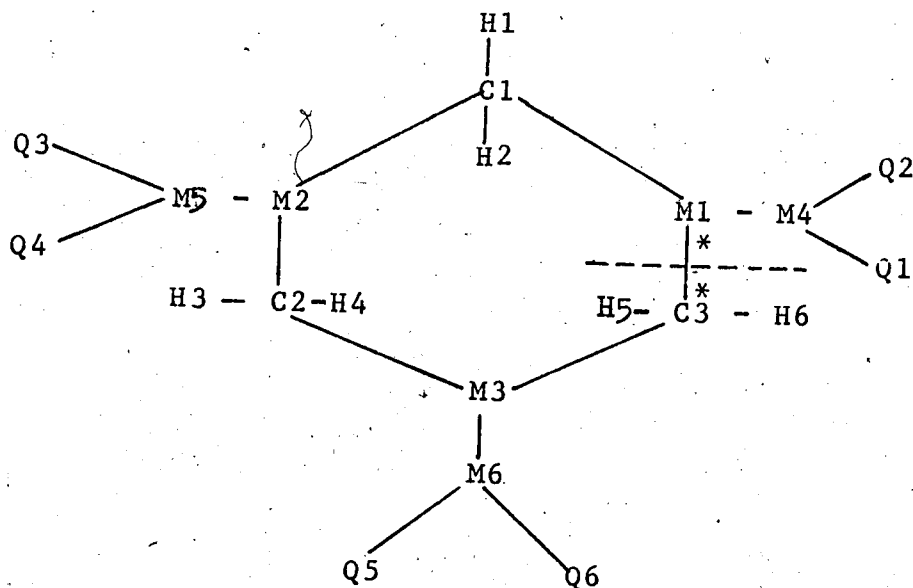


Figure 1

RDX Molecule in Two Dimensions

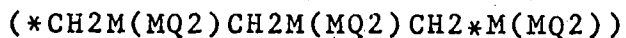
(b) If there are closed rings of atoms as in the case of RDX any bond in the ring is chosen and an unrecognized symbol such as (*) is written before

the symbol of each of the two atoms forming the bond. (Figure 1). The atoms chosen arbitrarily in this case are M1 and C3. Now the line indicating the bond can be removed because the connection between the bonded atoms is implied by the pair of unrecognized symbols (*). If the molecule contains more than one ring this procedure is repeated for all rings and finally a simply connected network of all atoms is obtained.

(c) A chain atom at the end of one chain is selected to be given the index number 1. (In this case C3) A left parenthesis is written and this left parenthesis is followed by the atomic symbol of the chosen chain atom. If the chain atom has an unrecognized symbol next to it, this symbol must be written down before the chain atom symbol. Next, the symbols of the side atoms connected to the preceding chain atom are written down using the multiplicity symbols 2 or 3 to indicate the side atoms of the same type. 2 hydrogens are connected to the chain atom C3. Continuing this way a branch point is reached. The chain atom M3 is connected to more than 2 chain atoms. It has a bond with C3, M6 and C2 chain atoms. Such a point is called a branch point. The branch containing M6 is a new chain. After writing

down the symbol of the chain atom M3 a left parenthesis is opened to point the beginning of a new chain and this parenthesis is followed by the first chain atom of the new chain which is M6. Following this, all other atoms of the new chain (Q5 and Q6) are written and the end of this subchain is marked with a right parenthesis. The next step is to return to previous chain (C2). At the end of the last chain a right parenthesis is written to enclose the whole formula.

In the light of the above discussion the symbolic formula for an RDX molecule can be written as follows:



An unrecognized symbol such as (*) can be used only for one bond.

CHAPTER IV

RESULTS AND CONCLUSIONS

As it was mentioned earlier, the crystal structure of RDX was determined by Choi and Prince⁴. The general x, y, z cartesian coordinates are provided in Table 3. The heat of formation of RDX was calculated using the program developed by Warshel and Levitt² and it was found out to be 390.53 kcal/gmole. The program gives the x, y, z cartesian coordinates of all the atoms in their final released states. These figures corresponding to general cartesian coordinates of Table 3 are also listed in Table 3. The program also provides diagonal core, bond, non-bond, repulsive, theta, phi and sublimation energy contributions to the total energy of the molecule; first derivatives with respect to x, y, z coordinates, bond lengths of the atoms involved, theta angles between three adjacent atoms, phi angles between four atoms, eigenvalues and eigenvectors for the initial and released states of the molecule; vibrational frequencies, vibrational enthalpy at room temperature, and zero point energy for the released state of the molecule. A single run of the program uses around 157 system seconds of

CDC computer system of Lehigh University.

As an initial step it was assumed that the initial breakup of this molecule would require the removal of an NO_2 group depending on Equation (2). There were two possibilities for the separation of NO_2 group. One of the possibilities was the movement of nitrogen atom between the two oxygen atoms and the second possibility involved the movement of NO_2 group as a whole.

The first possibility involved the movement of nitrogen atom away from O_2 group as a result of which the NO_2 group would be turned inside out. Sufficient movement of nitrogen atom would end up with the separation of this group. At this stage one of the three NO_2 groups had to be chosen to be removed. Two of the NO_2 groups are very similar, but the third one is quite different in the sense that N-N bond is shorter and the NO_2 group is at a smaller angle to the plane defined by three carbon atoms. Similar calculations which were proceeded earlier involved the removal of this group. During this study same group was chosen in order to compare the results easily. Using atom references from Figure 1, atom M6 was moved towards atom M3 and the heat of formation was calculated. First of all, the general x, y, z cartesian coordinates given in Table 3 are converted in such a way that the nitrogen atom M3 is located at the origin and y, z coordinates of M6 were zero. A movement of 0.15 Å of M6 towards M3 increased the heat of formation to

413.5 kcal/gmole. Then atom M6 was moved away from M3 while the positions of all other atoms in the molecule were fixed. The calculated values of the heat of formation are shown in Table 1 and Figure 2.

Initially, the crystal structure of RDX exerted a force on the molecule, and therefore a decrease in the heat of formation was observed. Later on, when M6 passed between the oxygen atoms Q5 and Q6 at about 2.1 Å displacement in x direction, the heat of formation was found out to be 433.03 kcal/gmole- higher compared to 390.53 kcal/gmole which is the heat of formation of RDX molecule in its original state. The energy continued to increase to a value of 445.21 kcal/gmole until point A of Figure 2 was reached at 2.3 Å. The difference between the energy at A and the initial state of RDX was 58.99 kcal/gmole. The energy then started to decrease with further outward movement of M6. A value of 390.11 kcal/gmole was obtained at a displacement of 2.5 Å. After this point, the heat of formation increased again since other atomic orbitals started to effect the calculations.

At 2.8 Å displacement of M6 the oxygen atoms Q5 and Q6 were also started to move outward from the rest of the molecule. If this was not the case, the energy might have exceeded the activation energy. While doing this, the relative displacement between the oxygen atoms were maintained. As the oxygen atoms started to move the energy increased first and

then started to decrease. After point C of Figure 2, another rapid increase of energy was prevented by moving the hydrogen atom H3. According to Equation (3) this hydrogen atom had to replace nitrogen atom M6. Therefore, after 3.0 Å displacement of M6, H3 was moved towards the place to occupy the position of M6. An increase of energy was observed until point D was reached at 3.20 Å displacement of M6 and after this point Q4 was also moved towards the position it would occupy if it replaced H3 as suggested by Equation (3).

The calculations were stopped at 3.30 Å displacement of M6 in the x direction. It may be interesting to go on with the similar type of calculations after this point to see the influence of other molecules of the crystal lattice, but there was not enough time to do this during this study.

The second possibility involved the movement of NO₂ group as a whole. In this case the maximum amount of energy observed was 453.81 kcal/gmole at 2.70 Å displacement of M6 atom in x direction. This means that the activation energy of 64.47 kcal/gmole was observed at 1.2 Å displacement of NO₂ group from its initial position. The results obtained by moving the NO₂ group as a whole are given in Table 3 and Figure 3. The energy started to decrease after this point. The calculations were stopped at 3.40 Å displacement of M6 from M3.

Figure 4 shows the comparison between the values obtained by moving M6 from M3 and the values obtained by moving

NO₂ from the rest of the molecule.

It can be seen that the amount of energy required to separate NO₂ group as a whole (64.47 kcal/gmole) is more than the energy required to move nitrogen away between the two oxygen atoms (58.99 kcal/gmole). The conclusion as a result of these two figures is that the separation of NO₂ can be achieved by moving the nitrogen between the two oxygen atoms and not by moving the NO₂ group as a whole.

The initial steps of the minimization procedure of Warshef and Levitt program² involves the Steepest Descent Method. After some steps of iteration by this method, the powerful Modified Newton-Raphson Method is applied. During this study it was not possible to obtain the convergence of Newton-Raphson Method. This problem was tackled by increasing the number of iterations of the Steepest Descent Method from the default value of 20 to 70. After 70 steps of iteration it was observed that the energy found remained unchanged for every calculation.

It must be noted that during this study only the removal of NO₂ group was observed. It is only the initial step in the reaction mechanism of RDX. The scope of this work can be extended to study the breaking down of the radicle according to Equation (3). Also other reaction mechanisms can be studied.

Also, as an another step, the influence of other molecules in the crystal structure of RDX can be studied.

TABLE 1

Heat of Formation as a Function of RDX Configuration

		Atom x, y, z Coordinates - Å						Heat of Formation Kcal/gmole
	M6	Q5	Q6	H3	Q4			
1	1.35, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		413.51	
2	1.32, 0.23, -0.12	1.95, 1.48, 0.02	2.17, -0.89, 0.05	-0.39, 2.24, -0.31	-1.26, 2.94, 1.91			
1	1.40, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		404.01	
2	1.33, 0.23, -0.12	1.95, 1.48, 0.01	2.17, -0.89, 0.05	-0.39, 2.24, -0.31	-1.26, 2.94, 1.91			
1	1.50, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		390.53	
2	1.33, 0.22, -0.11	1.96, 1.47, 0.03	2.18, -0.90, 0.04	-0.39, 2.24, -0.31	-1.26, 2.94, 1.91			
1	1.60, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		386.22	
2	1.34, 0.22, -0.11	1.97, 1.47, 0.04	2.18, -0.90, 0.04	-0.38, 2.24, -0.31	-1.25, 2.94, 1.91			
1	1.70, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		390.00	
2	1.34, 0.22, -0.12	1.97, 1.48, 0.01	2.18, -0.89, 0.05	-0.37, 2.24, -0.31	-1.25, 2.94, 1.90			
1	1.80, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		400.12	
2	1.35, 0.22, -0.10	1.97, 1.47, 0.06	2.19, -0.90, 0.05	-0.37, 2.24, -0.30	-1.25, 2.94, 1.91			
1	2.00, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		422.55	
2	1.36, 0.22, -0.10	1.99, 1.47, 0.04	2.20, -0.90, 0.04	-0.36, 2.25, -0.30	-1.23, 2.92, 1.92			
1	2.10, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		433.03	
2	1.37, 0.22, -0.10	2.01, 1.46, 0.03	2.21, -0.91, 0.04	-0.36, 2.25, -0.30	-1.24, 2.93, 1.92			
1	2.20, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		442.92	
2	1.37, 0.22, -0.10	2.01, 1.47, 0.02	2.22, -0.90, 0.06	-0.34, 2.24, -0.30	-1.24, 2.95, 1.92			
1	2.30, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		445.21	
2	1.38, 0.22, -0.10	2.01, 1.45, 0.04	2.22, -0.90, 0.06	-0.33, 2.24, -0.29	-1.23, 2.94, 1.91			
1	2.40, 0.00, 0.00	2.14, 1.15, 0.01	2.10, -1.17, 0.01	-0.14, 2.24, -0.13	-0.80, 2.68, 1.56		401.91	
2	1.38, 0.22, -0.10	2.02, 1.46, 0.04	2.23, -0.91, 0.06	-0.32, 2.24, -0.29	-1.23, 2.94, 1.91			

1	2	50	0.00	0.00	2.14	1.15	0.01	2.10	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	390.11
1	2	1.39	0.21	-0.09	2.02	1.46	0.04	2.23	-0.91	0.07	-0.32	2.24	-0.29	-1.22	2.94	1.91	
1	2	2.60	0.00	0.00	2.14	1.15	0.01	2.10	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	395.01
1	2	1.40	0.21	-0.09	2.03	1.46	0.04	2.24	-0.91	0.06	-0.31	2.24	-0.19	-1.22	2.94	1.91	
1	2	2.70	0.00	0.00	2.14	1.15	0.01	2.10	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	412.92
1	2	1.40	0.21	-0.09	2.04	1.46	0.04	2.24	-0.91	0.06	-0.30	2.24	-0.28	-1.23	2.95	1.91	
1	2	2.76	0.00	0.00	2.14	1.15	0.01	2.10	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	430.18
1	2	1.41	0.21	-0.10	2.04	1.46	0.04	2.25	-0.91	0.06	-0.30	2.24	-0.28	-1.22	2.95	1.91	
1	2	2.80	0.00	0.00	2.18	1.15	0.01	2.14	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	433.91
1	2	1.42	0.21	-0.09	2.05	1.46	0.04	2.25	-0.91	0.06	-0.30	2.24	-0.29	-1.21	2.94	1.91	
1	2	2.85	0.00	0.00	2.23	1.15	0.01	2.19	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	429.31
1	2	1.42	0.21	-0.09	2.06	1.46	0.03	2.27	-0.91	0.06	-0.28	2.24	-0.28	-1.22	2.95	1.91	
1	1	2.90	0.00	0.00	2.28	1.15	0.01	2.24	-1.17	0.01	-0.14	2.24	-0.13	-0.80	2.68	1.56	416.02
1	2	1.43	0.21	-0.10	2.07	1.46	0.03	2.28	-0.91	0.05	-0.27	2.24	-0.27	-1.22	2.95	1.91	
1	3	0.00	0.00	0.00	2.38	1.15	0.01	2.34	-1.17	0.01	0.00	2.09	-0.13	-0.80	2.68	1.56	408.89
1	2	1.46	0.19	-0.09	2.11	1.43	0.03	2.30	-0.94	0.05	-0.23	2.22	-0.25	-1.21	2.96	1.90	
1	3	0.05	0.00	0.00	2.43	1.15	0.01	2.39	-1.17	0.01	0.10	1.97	-0.13	-0.80	2.68	1.56	409.05
1	2	1.48	0.17	-0.10	2.13	1.41	0.03	2.31	-0.96	0.04	-0.20	2.21	-0.24	-1.20	2.96	1.90	
1	2	3.10	0.00	0.00	2.48	1.15	0.01	2.44	-1.17	0.01	0.15	1.91	-0.13	-0.80	2.68	1.56	424.42
1	2	1.49	0.16	-0.10	2.15	1.40	0.02	2.32	-0.97	0.04	-0.19	2.21	-0.23	-1.20	2.97	1.90	
1	3	0.20	0.00	0.00	2.58	1.15	0.01	2.54	-1.17	0.01	0.25	1.80	-0.13	-0.80	2.65	1.45	432.11
1	2	1.52	0.14	-0.09	2.19	1.37	0.02	2.34	-0.99	0.05	-0.15	2.19	-0.23	-1.19	2.98	1.86	
1	3	0.25	0.00	0.00	2.68	1.15	0.01	2.64	-1.17	0.01	0.30	1.73	-0.13	-0.80	2.65	1.40	427.13
1	2	1.54	0.12	-0.10	2.20	1.36	0.01	2.36	-1.02	0.04	-0.12	2.18	-0.22	-1.19	3.99	1.85	
1	3	0.30	0.00	0.00	2.74	1.15	0.01	2.74	-1.17	0.01	0.35	1.73	-0.13	-0.80	2.65	1.35	420.10
1	2	1.56	0.11	-0.10	2.23	1.34	0.01	2.37	-1.03	0.03	-0.10	2.17	-0.22	-1.19	3.01	1.83	

(1) Initial x, y, z coordinates.

(2) x, y, z coordinates after relaxation.

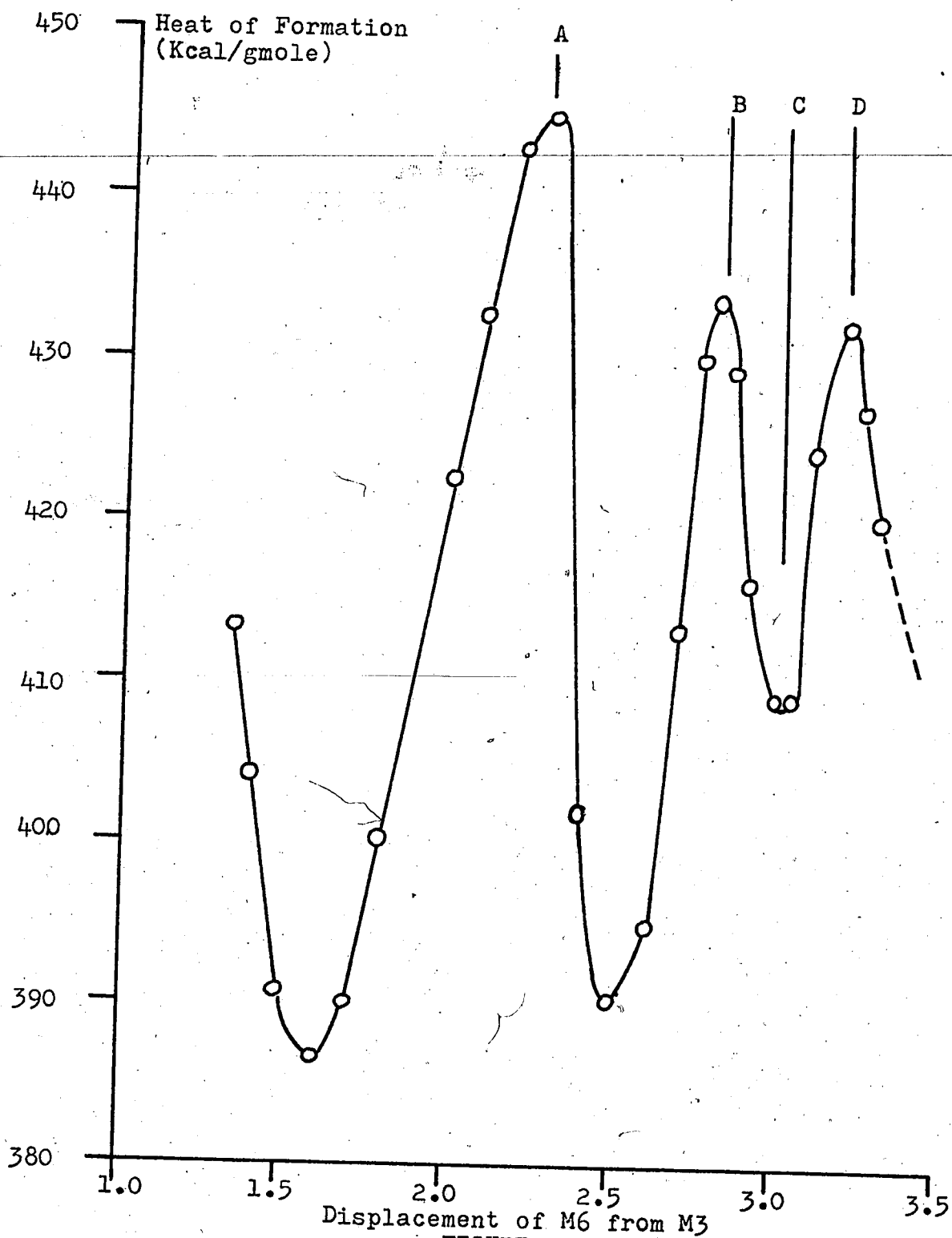


FIGURE 2
 Variation of the Heat of Formation of RDX as
 Nitrogen Atom M6 is Moved from M3

TABLE 2

Heat of Formation as Function of RDX Configurations
When NO₂ Group Moves as a Whole

Atom x,y,z Coordinates - Å				Heat of Formation Kcal/gmole
	M6	Q5	Q6	
1	1.35,0.00, 0.00	2.14,1.15, 0.01	2.10,-1.17,0.01	413.51
2	1.32,0.23,-0.12	1.95,1.48, 0.02	2.17,-0.89,0.05	
1	1.40,0.00, 0.00	2.14,1.15, 0.01	2.10,-1.17,0.01	404.01
2	1.33,0.23,-0.12	1.95,1.48, 0.01	2.17,-0.89,0.05	
1	1.50,0.00, 0.00	2.14,1.15, 0.01	2.10,-1.17,0.01	390.53
2	1.33,0.22,-0.11	1.96,1.47, 0.03	2.18,-0.90,0.04	
1	1.60,0.00, 0.00	2.24,1.15, 0.01	2.20,-1.17,0.01	398.22
2	1.34,0.22,-0.11	1.98,1.47, 0.04	2.19,-0.90,0.03	
1	1.70,0.00, 0.00	2.34,1.15, 0.01	2.30,-1.17,0.01	407.00
2	1.37,0.22,-0.12	2.00,1.47,-0.01	2.21,-0.90,0.04	
1	1.80,0.00, 0.00	2.44,1.15, 0.01	2.40,-1.17,0.01	413.12
2	1.39,0.22,-0.11	2.03,1.46,-0.02	2.22,-0.91,0.04	
1	1.90,0.00, 0.00	2.54,1.15, 0.01	2.50,-1.17,0.01	424.71
2	1.40,0.22,-0.12	2.05,1.46,-0.02	2.25,-0.91,0.04	
1	2.00,0.00, 0.00	2.64,1.15, 0.01	2.60,-1.17,0.01	429.16
2	1.42,0.22,-0.12	2.06,1.46,-0.01	2.26,-0.91,0.03	
1	2.10,0.00, 0.00	2.74,1.15, 0.01	2.70,-1.17,0.01	433.37
2	1.45,0.22,-0.11	2.08,1.47,-0.01	2.29,-0.90,0.03	
1	2.20,0.00, 0.00	2.84,1.15, 0.01	2.80,-1.17,0.01	436.83
2	1.46,0.21,-0.12	2.10,1.46,-0.01	2.30,-0.91,0.02	
1	2.30,0.00, 0.00	2.94,1.15, 0.01	2.90,-1.17,0.01	441.24
2	1.48,0.21,-0.12	2.12,1.45,-0.01	2.32,-0.92,0.02	
1	2.40,0.00, 0.00	3.04,1.15, 0.01	3.00,-1.17,0.01	445.11
2	1.50,0.20,-0.11	2.15,1.45,-0.01	2.34,-0.92,0.02	
1	2.50,0.00, 0.00	3.14,1.15, 0.01	3.10,-1.17,0.01	449.12
2	1.52,0.20,-0.12	2.16,1.45,-0.02	2.36,-0.92,0.01	
1	2.60,0.00, 0.00	3.24,1.15, 0.01	3.20,-1.17,0.01	451.87
2	1.53,0.20,-0.12	2.19,1.45,-0.02	2.38,-0.93,0.01	
1	2.70,0.00, 0.00	3.34,1.15, 0.01	3.30,-1.17,0.01	453.81
2	1.56,0.20,-0.12	2.21,1.44,-0.03	2.40,-0.93,0.01	
1	2.90,0.00, 0.00	3.54,1.15, 0.01	3.50,-1.17,0.01	451.46
2	1.60,0.20,-0.11	2.26,1.43,-0.03	2.43,-0.94,0.00	
1	3.00,0.00, 0.00	3.64,1.15, 0.01	3.60,-1.17,0.01	444.56
2	1.61,0.19,-0.11	2.28,1.43,-0.04	2.45,-0.95,0.00	
1	3.10,0.00, 0.00	3.74,1.15, 0.01	3.70,-1.17,0.01	439.61
2	1.63,0.19,-0.11	2.30,1.43,-0.04	2.47,-0.95,0.00	
1	3.20,0.00, 0.00	3.84,1.15, 0.01	3.80,-1.17,0.01	432.87
2	1.65,0.19,-0.11	2.32,1.42,-0.04	2.48,-0.95,0.00	
1	3.30,0.00, 0.00	3.94,1.15, 0.01	3.90,-1.17,0.01	427.75
2	1.67,0.19,-0.10	2.32,1.42,-0.04	2.50,-0.95,0.00	
1	3.40,0.00, 0.00	4.04,1.15, 0.01	4.00,-1.17,0.01	421.83
2	1.69,0.19,-0.10	2.37,1.42,-0.04	2.52,-0.96,0.00	

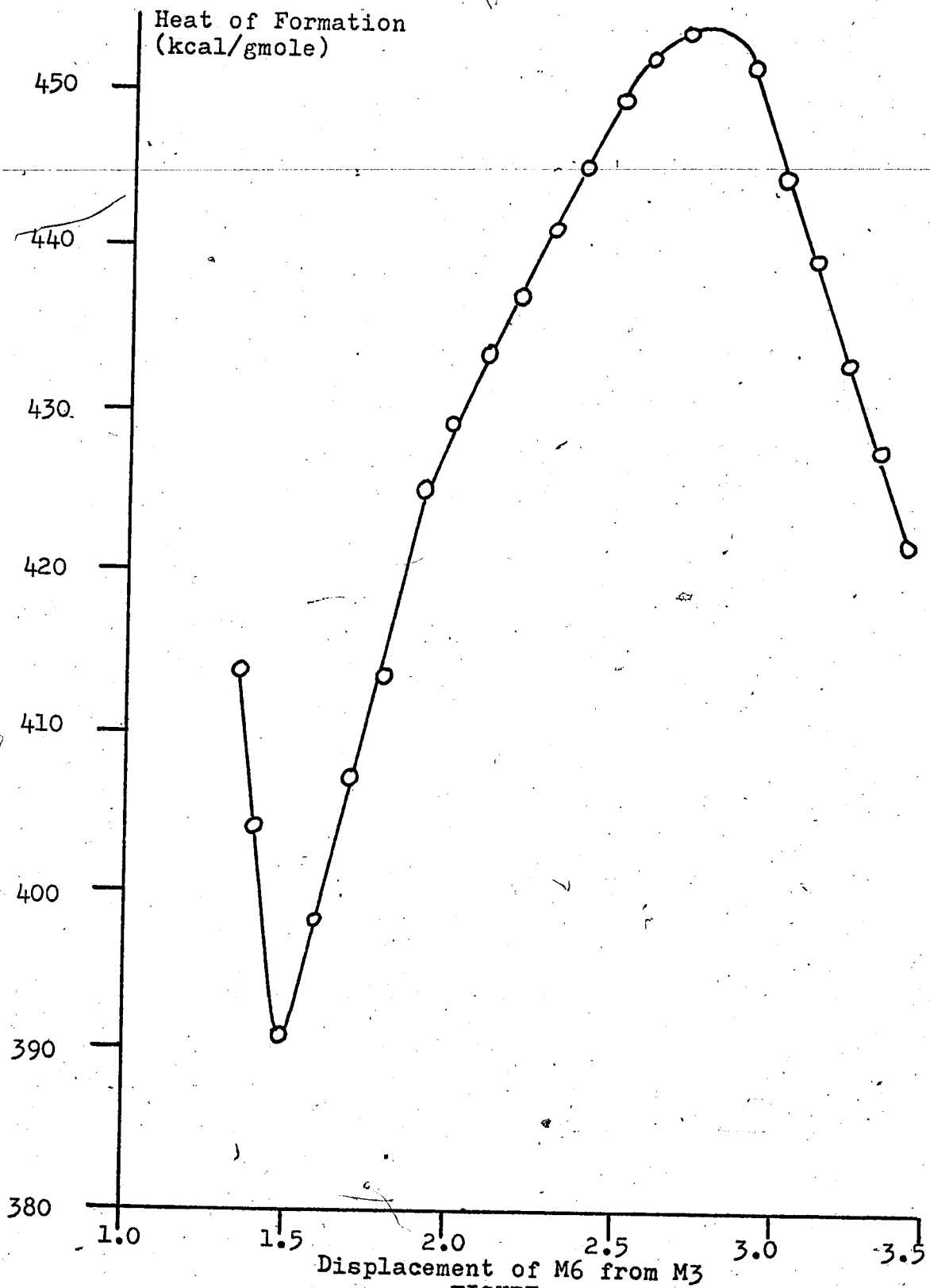


FIGURE 3
Variation of the Heat of Formation of RDX
as NO₂ is Moved From the Rest of the Molecule

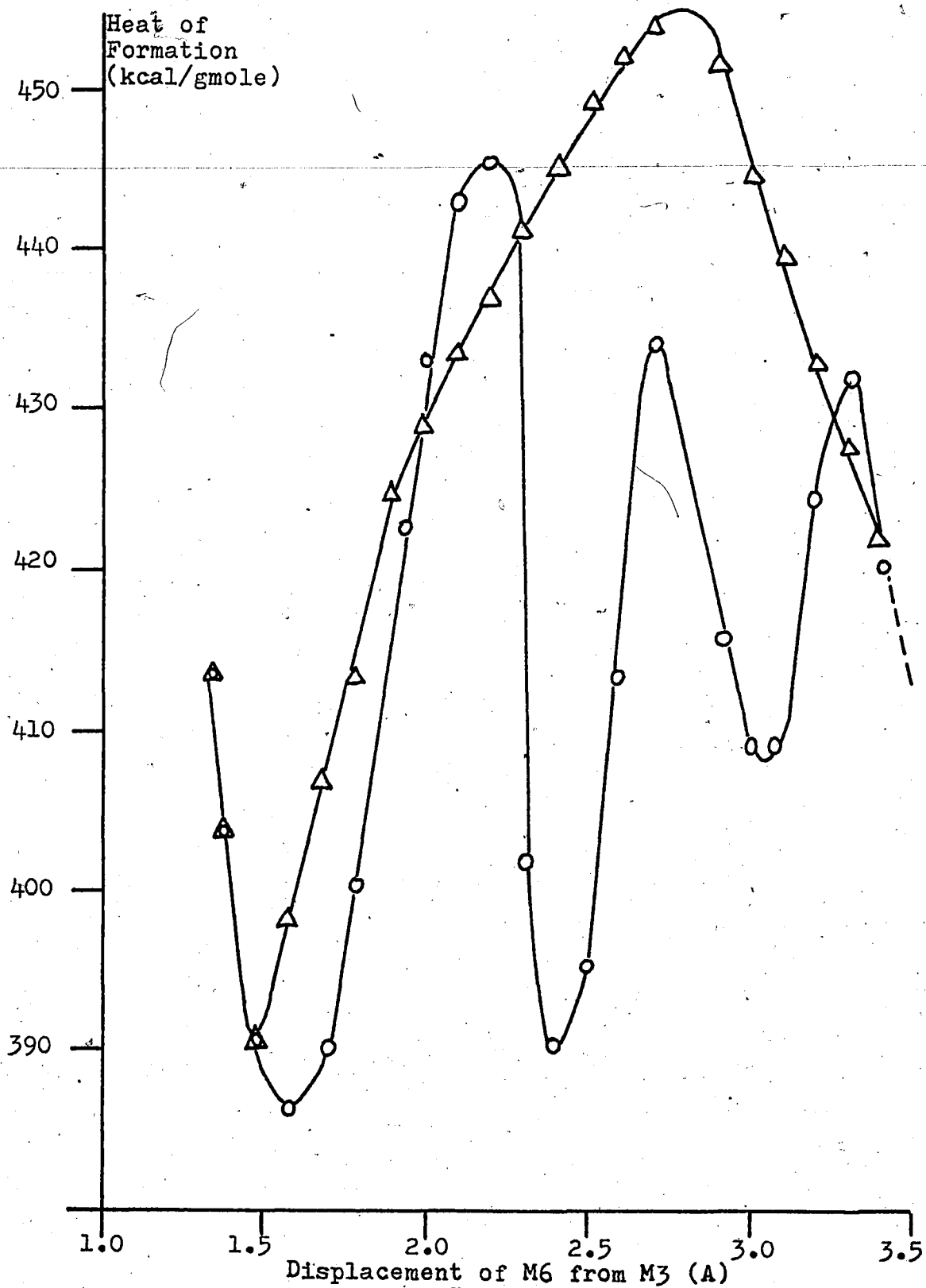


FIGURE 4

Variation of the Heat of Formation of RDX as M6 is Moved from M3 and as NO₂ is Moved from the Rest of the Molecule

TABLE 3

General x, y, z Cartesian Coordinates of RDX.

Atom	Atom x, y, z Coordinates - Å					
	Initial State			Released State		
	x	y	z	x	y	z
C3	1.9602	4.4132	2.3121	1.9896	4.4247	2.2693
H5	2.7049	3.6643	2.0529	2.6485	3.5919	1.9333
H6	1.8982	5.1296	1.5.32	1.9847	5.1394	1.4279
M3	0.7066	3.7291	2.4941	0.6004	3.8587	2.5022
M6	-0.4396	4.4849	2.2253	-0.4765	4.3804	2.0259
Q5	-1.4777	4.0903	2.6815	-1.7566	3.9555	2.4328
Q6	-0.3111	5.4294	1.4886	-0.4521	5.4576	1.1270
C2	0.6631	2.8241	3.6357	0.6021	2.8883	3.6598
H3	-0.3441	2.4502	3.7910	-0.3671	2.3808	3.7862
H4	1.3380	1.9999	3.4183	1.3218	2.0669	3.4313
M2	1.1561	3.4676	4.8587	1.0590	3.5886	4.9170
M5	0.2043	4.0798	5.6693	0.2497	3.9439	5.8532
Q3	-0.9135	3.6366	5.6351	-1.0992	3.5362	5.8706
Q4	0.5985	4.9433	6.4147	0.6316	4.8199	6.8803
C1	2.4242	4.1412	4.7119	2.4584	4.1541	4.7438
H1	3.1650	3.4074	4.5256	3.1642	3.2989	4.6395
H2	2.6535	4.7083	5.6158	2.7817	4.6790	5.6597
M1	2.3214	5.0463	3.5661	2.6262	5.0484	3.5135
M4	2.9791	6.2257	3.5832	3.0891	6.2285	3.5558
Q1	2.9923	6.8657	2.5573	3.1297	7.0698	2.4238
Q2	3.4919	6.5821	4.6456	3.5865	6.8074	4.7430

REFERENCES

1. A. Warshel and M. Karplus, J. Am. Chem. Soc., 94, 5612, (1972).
2. A. Warshel and M. Levitt, QCPE 247, Quantum Chemistry Program Exchange, Indiana University.
3. A. Lappicirella and A. Warshel, Calculations of Ground and Excited State Potential Surfaces for Heteroatom Conjugated Molecules, unpublished.
4. C. S. Choi and E. Prince, Acta Cryst., B28, 2857, (1972).
5. J. D. Cosgrove and A. J. Owen, Chem. Comm., 286 (1968).
6. J. D. Cosgrove and A. J. Owen, Comb. and Flame, 22, 13 (1974).
7. A. J. B. Robertson, Trans. Faraday Soc., 45, 85 (1949).

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8. F.C.Rauch and A.J.Fanelli, J.Phys.Chem., 73, 1604, (1969).
 9. E.Clementi, J.Chem.Phys., 46, 4731, (1967).

 10. E.Clementi, H.Clementi, and D.R.Davis, J.Chem. Phys., 46, 4725, (1967).
 11. E.Clementi, J.Chem.Phys., 46, 4737 (1967).

V I T A

Mehmet Ali Baran was born in Istanbul, Turkey in 1954. His father, Hasan Baran works as an attorney in Izmir and his mother is Zeliha Baran.

After finishing high school in Ankara in 1972, Mehmet Ali Baran attended Boğaziçi University in Istanbul where he received B.S. and M.S. degrees in Chemical Engineering in 1976 and 1978. He also received a B.S. in Mathematics as a double major in 1978. Then, he started Lehigh University in Fall 1978 as a candidate for Master's Degree in Mechanical Engineering. He worked as a teaching assistant during his graduate work in Boğaziçi University, and as a research assistant during his studies in Lehigh University.