

Molecular Orbital Study of the Electronic Structure and Spectrum of Hexahydro-1,3,5-trinitro-s-triazine

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Molecular orbital calculations (CNDO) have been utilized in a study of the electronic structure and ultraviolet absorption spectrum of hexahydro-1,3,5-trinitro-s-triazine (RDX). The vacuum uv absorption spectrum of RDX in acetonitrile has been measured from 3600 to 1840 Å. Prominent absorption maxima are observed at 2360 Å (ϵ 11,000 M^{-1} cm $^{-1}$) and at 1955 Å (ϵ 16,400 M^{-1} cm $^{-1}$). These bands are assigned as $\pi \rightarrow \pi^*$ transitions localized on the nitro groups on the basis of the MO calculations.

I. Introduction

The title compound (RDX) has been the subject of continued interest because of its use as a secondary explosive.¹⁻³ In conjunction with present efforts in these laboratories to study the mechanism of decomposition of this material, we have carried out all valence-electron molecular orbital calculations on four different conformations of RDX in order to obtain information concerning the electronic structure and spectrum of the molecule. The atomic charge densities, overlap populations, and total ground-state energies have been obtained for these conformers and the results have been related to experimental observations. We have also measured the vacuum uv spectrum of RDX in the region from 3600 to 1840 Å and assigned the observed transitions with the aid of the MO calculations.

II. Experimental Section

Pure RDX was supplied by Dr. B. Suryanarayana of the Explosives Laboratory, Picatinny Arsenal, Dover, N. J. This material was purified from military grade RDX (Holston Defense Corp.) by recrystallization from γ -butyrolactone, to remove most of the octahydro-1,3,5,7-tetranitro-s-tetrazine (HMX) impurity, followed by three recrystallizations from aqueous acetone. The purified RDX was supplied to us under ethanol. Before use the RDX was filtered and dried for 16 hr at 60° under vacuum. The melting point of the final material was found to be 204.5–205° dec as measured on a calibrated microscope hot stage. A purity of greater than 99.5% was determined by a chromatographic analysis using the procedure of Rowe.⁴ This material was stored in the dark and dried by the procedure given above prior to this spectral investigation.

The absorption spectrum of RDX in Eastman spectrograde acetonitrile was measured from 3600 to 2000 Å using a Cary Model 14R spectrophotometer and from 2400 to 1840 Å using a Jarrell-Ash nor-

mal-incidence vacuum spectrometer. The vacuum ultraviolet instrumentation and slit width have been described previously.⁵ The cells employed in this investigation were of fused quartz with path lengths of 0.1 and 2 cm and of stainless steel with MgF₂ windows (2 mm thick—Harshaw Chemical Co.) and path length of 0.078 cm. The concentrations of RDX solutions were between 9.1×10^{-3} and 4.0×10^{-3} M.

Two to four determinations of absorbance were recorded every 10 Å over the spectral region 1840–3600 Å and the data presented as molar extinction coefficient (ϵ) in units of M^{-1} cm $^{-1}$ vs. wave number in kK ($\text{cm}^{-1} \times 10^3$). The variation in ϵ was less than $\pm 5\%$.

III. Calculations

The MO method used in this study is the CNDO/2 treatment developed by Pople and coworkers.⁶ In this semiempirical treatment, all the valence electrons in a molecule are taken into account explicitly, so that in the case of RDX there are 84 electrons distributed among 66 atomic orbitals. For the calculation of ground-state properties, we have used the MO parameters suggested by Pople and Segal;⁶ therefore, the only input data necessary to perform the calculations are the coordinates of the atoms in the molecule.

The positional coordinates of the carbon, nitrogen, and oxygen atoms for RDX in the crystalline phase have been determined by X-ray diffraction.⁷ The

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molecule was found to be in a chair conformation with two of the N-N bonds (1.41 Å) almost parallel to one another and roughly perpendicular to the "average plane" of the ring atoms, whereas the third N-N bond (1.36 Å) was found to be in a direction lying in this "plane."⁷ No information appears to be available on the precise structure of RDX in the liquid or vapor phase.

In this theoretical study, we performed MO calculations on the RDX molecule in the following four conformations.⁸ (1) The chair form corresponding to the experimentally determined structure of RDX in a crystalline state.⁷ (2) An idealized chair form in which the three C₂N-NO₂ groups are (individually) planar as found for crystalline HMX and a threefold molecular symmetry is assumed; bond lengths and angles are average values taken from RDX⁷ and HMX.⁹ (3) A chair form identical with (2) above, except the three NO₂ groups are rotated 90° about each N-N bond. (4) A boat conformer derived from (2) above with carbon and nitrogen atoms placed bow and stern.

IV. Results and Discussion

1. *Ground State.* The theoretically calculated electronic charge distribution is essentially the same for each of the four conformations of RDX studied. In Table I we list the calculated atomic charge densities

Table I: Calculated Atomic Charge Densities in RDX

| Atom ^a | Charge | Atom ^a | Charge |
|-------------------|--------|-------------------|--------|
| 1 | -0.170 | 4 | 0.212 |
| 2 | 0.573 | 5 | 0.047 |
| 3 | -0.329 | 6 | -0.005 |

^a See Figure 1 for the numbering of the atoms in RDX conformer 2.

found for conformer 2, which is the most convenient to report because of the threefold symmetry (see Figure 1 for the numbering of the atoms in the molecule). A point of interest here is the relatively high positive charge ($q = +0.21$) on the carbon atoms and the negative charge ($q = -0.33$) on the oxygen atoms. This result is consistent with the proposed mechanism for the decomposition of RDX (in the liquid phase) which involves either intra- or intermolecular carbon-oxygen interaction.¹⁻³ It is also consistent with the short intermolecular C...O contact distance of 3.21 Å in crystalline RDX, which we have calculated from the X-ray diffraction data in ref 7. This short contact distance compared to the 3.4 Å obtained from the sum of van der Waals radii implies a strong attractive force between the carbon and oxygen atoms. As in the case of crystalline HMX,⁹ the C...O contact is not in line with any C-H bond direction, and is therefore not a "hydrogen bond."

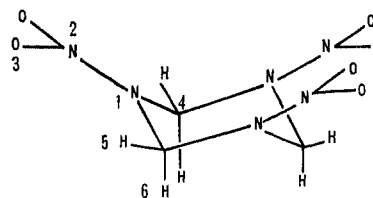


Figure 1. Numbering of the atoms in RDX (conformer 2).

Although the electronic charge densities are the same in the four RDX conformers studied, the calculated dipole moments are quite different because of geometrical considerations. The calculated dipole moments for conformers 1, 2, 3, and 4 are 7.76, 4.96, 4.45, and 1.08 D, respectively. The value for the dipole moment of nitramine in dioxane is 3.75 D;¹⁰ however, we are not aware of any experimental value for the dipole moment of RDX itself.

The calculated overlap populations were also found to be insensitive to conformational changes and, as in the case of charge densities, we may consider the results obtained for conformer 2. Overlap populations obtained from MO calculations may be used to estimate bond energies by establishing a curve of overlap population *vs.* bond energy for molecules containing the atom pair under study.¹¹ In order to obtain such a calibration curve for the N-N bond, calculations were performed on N₂H₄, N₂H₂, and N₂. The resultant overlap populations, along with the experimental bond energies, are presented in Table

Table II: Calculated Overlap Populations and Observed Bond Energies for Compounds Containing N-N Bonds

| Molecule | N-N bond overlap pop. | N-N bond energy, kcal/mol |
|-------------------------------|-----------------------|---------------------------|
| N ₂ H ₄ | 0.55 ^a | 60 ^c |
| N ₂ H ₂ | 0.91 ^a | 109 ^d |
| N ₂ | 1.33 ^a | 225 ^c |
| RDX | 0.62 ^b | 66 ^e |

^a MO calculations were carried out on molecules built from standard bond lengths and angles given in J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967). ^b Conformer 2. ^c T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths and Co. (Publishers) Ltd., London, 1958, p 278. ^d "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1965. ^e Extrapolated from curve of overlap population *vs.* bond energy for N₂H₄, N₂H₂, and N₂ molecules.

(8) The x , y , z positional coordinates of the atoms in the RDX conformers, which were used in the calculations, are available from the authors upon request.

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(10) E. C. E. Hunter and J. R. Partington, *J. Chem. Soc.*, 309 (1933).

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II. A value of 66 kcal/mol is obtained for the energy of the N-N bond in RDX from the calibration curve. A bond energy of this magnitude correlates reasonably well with the limited kinetic data obtained in these laboratories on the gas-phase decomposition of RDX in which the rate-controlling step is the homolytic rupture of the N-N bond.³ The calculated value of the overlap population for the N-N bond in RDX indicates that this bond possesses some double-bond character. The overlap population for the C-N bond in RDX is found to be equal to that (0.67) calculated for the model single-bond compound $\text{H}_3\text{C-NH}_2$ and a bond energy of 80 kcal/mol¹² is therefore estimated for the C-N bond in RDX.

The theoretically calculated total energies of RDX vary with conformation and the results are shown in Table III. It is the difference between the cal-

Table III: Calculated Total Energy of RDX Conformers

| Conformer ^a | E , kcal/mol |
|------------------------|-------------------|
| 1 | -129,951 |
| 2 | -129,958 |
| 3 | -129,927 |
| 4 | -129,958 |

^a See section III for description of conformers.

culated energies and not their absolute values which is of significance in this work. Moreover, the more negative energies correspond to more stable conformations. The results of the MO calculations in RDX indicate that the structure observed in the crystal (conformation 1) is energetically less favorable than either conformation 2 or 4 by 7 kcal/mol. It should be noted, however, that the quantum mechanical calculations are carried out on the isolated molecule and thus the theoretical results should be compared with measurements made on the molecule in the gas phase. In general, significant changes in conformation may be brought about by packing forces in the crystal which are absent in the gas and liquid. Such a phenomenon has been observed for molecules such as diboron tetrachloride (which is eclipsed in the crystal and staggered in the vapor)¹³ and biphenyl (in which the two phenyl rings are nearly planar in the crystal and progressively more skewed in the liquid and vapor).¹⁴ In the case of crystalline RDX, it is reasonable that the additional forces due to crystal packing account for more than 7 kcal/mol. Therefore, the calculations predict that the conformation of RDX in the liquid and vapor has a higher degree of symmetry than that observed in the crystal. The ground-state calculations indicate that the boat and chair 2 conformers are equally stable and, there-

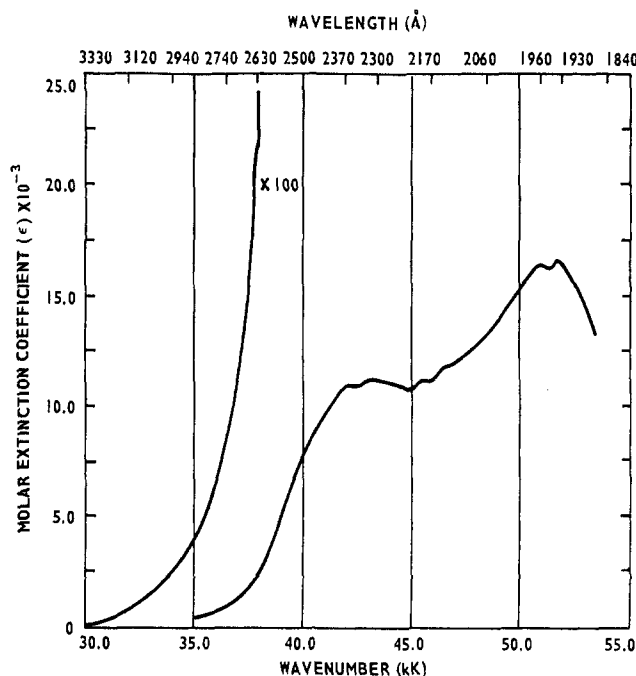


Figure 2. Vacuum ultraviolet absorption spectrum of RDX in acetonitrile.

fore, equally probable. We will return to this point later in conjunction with the calculated electronic spectrum.

From a consideration of the results in Table III for conformers 2 and 3, a rotational energy barrier of approximately 10 kcal/mol ($(1/3)[-129,927 - (-129,958)]$) is predicted for the rotation of an NO_2 group about the N-N bond in RDX. Additional calculations on intermediate angles of twist were not attempted due to the large computational times involved for a molecule of this size.

2. *Excited States.* The absorption spectrum of RDX in acetonitrile is shown in Figure 2 as molar extinction coefficient ϵ vs. wave number. Two distinct absorption bands are seen at 2360 Å (ϵ 11,000 $\text{M}^{-1} \text{cm}^{-1}$) and at 1955 Å (ϵ 16,400 $\text{M}^{-1} \text{cm}^{-1}$) with weak vibrational structure superimposed on each band. The 2360-Å band is less distinct and the spectrum is similar to that reported by Jones and Thorn¹⁵ when the data are plotted as $\log \epsilon$ vs. wave number. The spectrum reported by Jones and Thorn was not extended far enough into the uv to observe the second band maximum. Stals, Barraclough, and Buchanan¹⁶ have reported the absorption spectrum of RDX in

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(13) E. B. Moore, Jr., *J. Chem. Phys.*, **43**, 503 (1965).

(14) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, Inc., New York, N. Y., Chapter 12.

(15) R. N. Jones and G. D. Thorn, *Can. J. Res.*, **278**, 828 (1949).

(16) J. Stals, C. G. Barraclough, and A. S. Buchanan, *Trans. Faraday Soc.*, **65**, 904 (1969).

acetonitrile and several other solvents. Our results agree with those of Stals, *et al.*, on the energy of the longer wavelength maximum at about 2360 Å; the location of the higher energy band at 1955 Å was made possible through the use of the vacuum uv instrumentation.

The CNDO/2 method cannot be used successfully to study electronic spectral transitions unless the theory is modified in some way. In this study, we have used the modifications introduced by Del Bene and Jaffé¹⁷ including configuration interaction due to the 25 lowest singly excited states to calculate the absorption spectrum of RDX in conformations 2 and 4. The calculated spectral transition energies are almost identical for conformers 2 and 4 indicating that the nitramino groups are effectively insulated and are not conjugated with the ring. The only difference in the two calculated spectra is the ratio of the oscillator

strengths, f , of the two strong transitions. This ratio is 0.7 for conformer 2 and 1.0 for conformer 4. Inasmuch as the ratio of observed extinction coefficients is 0.67, the results suggest that the chair conformer 2 is the one actually found in solution or in the gas phase and accordingly we report the results calculated for that conformer along with the experimental values in Table IV. Although the calculated energies are only in fair agreement with experiment, the pattern of f values makes the assignments of the transitions straightforward. From an analysis of the MO wavefunctions, the two prominent absorption bands observed at 2360 and 1955 Å are assigned as absorptions arising primarily from $\pi \rightarrow \pi^*$ transitions localized on the nitro groups. In addition, we conclude that there are weak $n \rightarrow \pi^*$ absorption bands buried in the 2360-Å band which result from promotion of the nonbonding electrons on the oxygen atoms.

In conclusion it should be noted that Stals, Barraclough, and Buchanan carried out VESCF CI calculations on N,N-dimethyl nitramine and extended their results to the excited states of RDX.¹⁶ Our MO calculations on RDX confirm the validity of their approach to the interpretation of the spectrum and support their assignments with a minor exception. We assign the first excited singlet state of RDX to an n, π^* transition rather than to an n, σ^* state; although, as pointed out by Stals, *et al.*, the π , n , and σ orbitals are intimately mixed in nitramino type molecules. The assignment of the lowest excited singlet state as an n, π^* state (as opposed to a π, π^* state) is consistent with the failure to observe fluorescence from RDX.¹⁶

Acknowledgment. This research was supported by Picatinny Arsenal, U. S. Army Munitions Command.

(17) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 4050 (1968).

Table IV: Calculated and Observed Spectral Transitions in RDX

| Calcd ^a | | | Obsd | |
|--------------------|-------|--------------------------|------------------|--|
| λ , Å | f | Type ^b | λ , Å | ϵ , $M^{-1} \text{ cm}^{-1}$ |
| 2165 | 0.006 | $n \rightarrow \pi^*$ | 2740 | 900 |
| 1997 | 0.005 | $n \rightarrow \pi^*$ | | |
| 1970 | 0.16 | $n \rightarrow \pi^{*c}$ | 2640 | 2,100 |
| 1969 | 0.01 | $\pi \rightarrow \pi^*$ | | |
| 1903 | 0.79 | $\pi \rightarrow \pi^*$ | 2360 | 11,000 |
| 1896 | 1.13 | $\pi \rightarrow \pi^*$ | 1955 | 16,400 |

^a Calculated for conformer 2. ^b The assignment shown in this column represents the leading term in the configuration interaction wave function. ^c Although this transition is predominantly $n \rightarrow \pi^*$, there is a 12% contribution from a $\pi \rightarrow \pi^*$ intramolecular charge transfer (nitramino N to the NO₂ group) which enhances the f value.