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# Electronic Structure Investigation and Nuclear Quadrupole Interactions in *β*-HMX

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The nuclear quadrupole coupling constants ($e^2qQ$) and asymmetry parameters ($\eta$) for the $^{14}$N nuclei in the $\beta$-HMX molecule are investigated by the Hartree−Fock−Roothaan variational procedure. For the two pairs of equivalent nuclei in the ring positions, the theoretical values are found to be −5.936 and −6.069 MHz for $e^2qQ$ and 0.432 and 0.490 for $\eta$, which are in good agreement with the corresponding experimentally observed magnitudes of 5.791 and 6.025 MHz for $e^2qQ$ and the values 0.4977 and 0.5180 for $\eta$ obtained from single-crystal measurements by the nuclear quadrupole resonance technique. Possible factors that could further improve the already close quantitative agreement between theory and experiment are also discussed. For the $NO_2$ groups in the peripheral positions the calculated values for $e^2qQ$ were found to be 1.442 and 1.369 for the two pairs of equivalent $^{14}$N nuclei, substantially smaller than for the ring nuclei, while for $\eta$ the corresponding values of 0.553 and 0.571 are close to those for the ring nuclei. Experimental values obtained for the magnitudes of $e^2qQ$ for $^{14}$N in the $NO_2$ groups are found to be 0.840 and 0.806 MHz, the corresponding $\eta$ being 0.42 and 0.48. Reasons for the weaker agreement with experiment, in contrast to the case of ring $^{14}$N nuclei, are suggested, the principal one being the possibility of strong intermolecular bonding between the oxygen ligands of the $NO_2$ groups and hydrogens in neighboring molecules. Calculated values of $e^2qQ$ and $\eta$ for $^{17}$O and $^2$H are presented for the $\beta$-HMX molecule with the hope that experimental values will become available for them in future for comparison with theory, allowing one to test whether the intermolecular interactions between oxygen and hydrogen atoms also influence their nuclear quadrupole interaction parameters.

## I. Introduction

The material $\beta$-HMX (cyclotetramethylenetetranitramine, $C_4H_8N_8O_8$), which is stable at room temperature among the four polymorphic phases[1] of HMX, is one of the most important energetic nitramines, obtained as a byproduct of RDX. The understanding of the properties of this highly energetic material are of great current interest. The property we focus on here is the nuclear quadrupole interaction associated with the various nuclei in this molecule, especially $^{14}$N. In recent years there is considerable effort being made[2] to use $^{14}$N as a sensor for detection of highly energetic materials using nuclear quadrupole resonance (NQR) spectroscopy.[3] The NQR signals associated with the various nuclei depend upon the electron distributions in the vicinity of those nuclei. In particular, the NQR signals for the ring and peripheral nitrogens in $\beta$-HMX have been studied[4,5] experimentally, providing an opportunity for theorists to test the ability of electronic wave functions obtained through first-principles quantum mechanical procedures to provide a quantitative understanding of the electric field gradient (efg) tensors associated with these $^{14}$N nuclei.

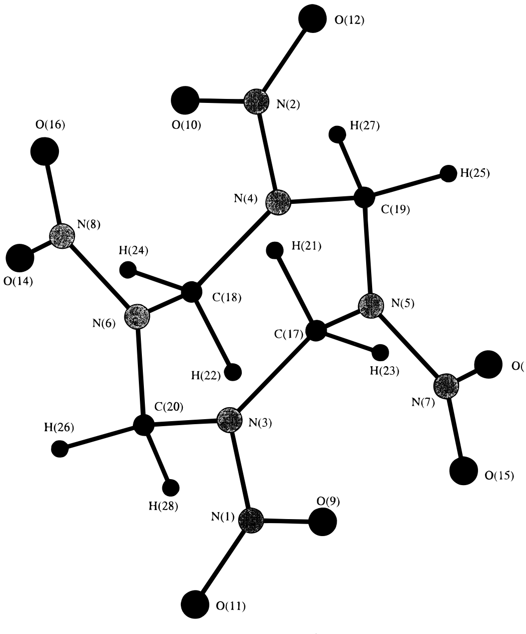

**Figure 1.** Atomic arrangement in the $\beta$-HMX molecule based on the crystal structure data in ref 6.

In $\beta$-HMX, shown in Figure 1, which has 28 atoms with alternate $CH_2$ and $N{-}NO_2$ groups in the ring, there are four $^{14}$N nuclei in the ring and four peripheral $^{14}$N associated with the $NO_2$ groups. But, because of the $C_2$ type (rotation by 180°) rotational symmetry[6] about the line joining the atoms N(3) and N(4), the eight $^{14}$N nuclei can be grouped into four pairs, two each in the ring and peripheral $NO_2$ groups, each pair containing two equivalent $^{14}$N nuclei. Experimentally, nuclear quadrupole interaction parameters ($e^2qQ$ and $\eta$) have been measured[4] for ring nitrogens consisting of the pairs of equivalent nuclei (N3,-N4) and (N5,N6) by the conventional NQR technique. The much smaller nuclear quadrupole interaction parameters for the two pairs of equivalent nuclei (N1,N2) and (N7,N8) in the $NO_2$ groups have been measured[5] through the use of special double-resonance techniques.[7,8] The quadrupole coupling constant ($e^2qQ$) and asymmetry parameter ($\eta$) within each of the four

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pairs are equal because the corresponding nitrogens are related to each other by the $C_2$ rotational symmetry in the crystal structure.[6] For the two sets of ring nuclei (N3,N4) and (N5,N6), termed equatorial and axial respectively, the magnitudes of $e^2qQ$ from NQR measurement have been determined[4] to be 5.791 and 6.025 MHz respectively, the corresponding asymmetry parameters ($\eta$) being 0.4977 and 0.5189. The experimental assignments[4] of these NQR signals to the two pairs of ring $^{14}$N nuclei have been based on the temperature dependences of the NQR frequencies. The different temperature dependences of the two NQR frequencies for the two sets of ring $^{14}$N nuclei have been utilized, in conjunction with the expected relative strengths of intermolecular bonding for the corresponding nitrogen atoms, to make complete assignments of the NQR frequencies.[4] This is in contrast to the case of RDX,[9] where there are three different ring $^{14}$N nuclei and three observed NQR frequencies, but complete assignment of the frequencies was not possible because for two of these frequencies, the temperature dependences were not significantly different from each other. From the assignments for the ring $^{14}$N nuclei in $\beta$-HMX, it has been observed[4] that the magnitude of $e^2qQ$ and the value of $\eta$ for the axial nitrogens (N5,N6) are slightly higher than those of $e^2qQ$ and $\eta$ for the equatorial nitrogens (N3,N4). For the $^{14}$N nuclei in the $NO_2$ groups (N1,N2) and (N7,N8), two sets of NQR frequencies[5] have been observed by a special resonance technique[7] leading to two values of $e^2qQ$ of 0.840 and 0.806 MHz and corresponding values of $\eta$ of 0.42 and 0.48, respectively. No assignments of these parameters have been made experimentally to the two pairs of equivalent nuclei.

A quantum mechanical study[10] of the electronic structure of $\beta$-HMX is thus helpful not only to have a broader knowledge about the electron distribution in this system and see if one can verify the observed assignments of NQR signals to the various ring $^{14}$N nuclei and explain the observed features of relative sizes of $e^2qQ$ and $\eta$ but also to compare quantitatively the theoretical and observed quadrupole coupling constants and asymmetry parameters. We have also investigated the coupling constants and asymmetry parameters for the $^{14}$N nuclei in the peripheral nitrogens from the $NO_2$ group, to compare them with the observed values and attempt assignments of the latter to the two pairs of equivalent nuclei. The values of $e^2qQ$ and $\eta$ for the deuteron ($^2$H) and $^{17}$O nuclei have also been obtained in this work, with the expectation that they will become available through future experimental investigations, either by nuclear magnetic resonance (NMR)[11] or other techniques.[7,8] A comparison of the measured $e^2qQ$ and $\eta$ with our theoretical predictions should be helpful in providing a more complete understanding of the electron distribution in this system. This understanding would be useful for the theoretical analysis of more complex phenomena, such as intermolecular interactions, which one expects to influence not only the values of $e^2qQ$ and $\eta$ for the nuclei of the atoms either directly or indirectly involved in these interactions but also the temperature dependences of the $e^2qQ$ and $\eta$, as well as spin−lattice relaxation effects.

For our investigations here, we have used the variational Hartree−Fock−Roothaan procedure[12] to study the electronic structure of $\beta$-HMX molecule. As is common practice at the present time, Gaussian basis functions[13] centered about various atoms have been used for the variational calculation. Recently this procedure has been applied successfully[14] by our group and others to study the nuclear quadrupole interactions in a variety of molecular and solid state systems.

In section II, we have briefly presented the procedure used in our investigation, our results and discussions being presented in section III. Section IV gives a summary of the results of our investigation and the main conclusions.

## II. Procedure

As mentioned in the preceding section, we have made use of the Hartree−Fock−Roothaan variational method to obtain the electronic energy levels and the wave functions for the $\beta$-HMX molecule. We shall not discuss this procedure in great detail here, since it has been described extensively in the literature.[12−14] Only a few pertinent points relevant to our present investigations will be discussed. Since the $\beta$-HMX molecule involves an even number of electrons, with no unpaired spin electrons, it is sufficient to use the restricted Hartree−Fock approximation with the same spatial molecular orbital wave functions for both spin up and spin down states for paired spin states. Also as is customary in current electronic structure investigations, linear combinations of Gaussians, referred to as contracted Gaussian basis functions in the literature,[13] are employed in our investigations, the use of Gaussian functions allowing economy in computing efforts through efficient evaluation of the multicenter integrals involved. For our calculations, we have used the Gaussian 92 set of programs.[13]

The arrangement of atoms in the $\beta$-HMX molecule, based on structural data from single-crystal X-ray and neutron diffraction measurements,[6] is shown in Figure 1. This molecule, which has four alternate $CH_2$ and $N-NO_2$ groups in a ring has, as mentioned earlier, exact $C_2$ type rotational symmetry about the line joining the two equatorial nitrogens N3 and N4 shown in the Figure 1. The $N-NO_2$ groups are planar, the carbon atoms have essentially tetrahedral symmetry around them, and the ring nitrogens have nonplanar configurations of nearest neighbor atoms, but the departure from planarity is less than that associated with bond angles characteristic of tetrahedral type coordination of each ring nitrogen with its three neighbors and a lone pair of electrons, essentially localized on the nitrogen atom. For our variational calculations, we have used a number of different basis sets. One of the extensive variational basis sets we have used in obtaining the molecular orbitals to accomodate 152 electrons in $\beta$-HMX is D95v, referred to as the valence double $\zeta$ basis set[15] comprised of 196 basis functions based on 532 primitive Gaussians. Following this, we have used an even more extensive basis set[10,13] called D95, increasing the number of basis functions to 216, based on 512 primitive Gaussians. To test the convergence of our results with respect to the size of the basis set, we have uncontracted[10] for the D95 basis set, the outermost p basis functions for C, N, and O atoms, which contribute most to the efg tensors at the nuclei, thus increasing the total number of basis functions to 276. This uncontracted basis set[10] is referred to as D95u. Additionally, we have used another extensive basis set referred to as 6-311g in the literature,[16] which has 284 basis functions and 560 primitive Gaussians. A comparison of the results we have found for the efg tensors at the nuclei for the different basis sets used shows good convergence with respect to basis set size, as will be discussed in section III.

For the efg tensor components at the different nuclei, we have made use of the following[3] expression for the various components, namely

$$V_{jk} = \sum_N \zeta_N \frac{(3R_{jN}R_{kN} - R_N^2\delta_{jk})}{R_N^5} - 2\sum_\mu \langle\psi_\mu| \frac{3r_j r_k - r^2\delta_{jk}}{r^5} |\psi_\mu\rangle \tag{1}$$

where the first term on the right represents the contribution to

**TABLE 1: $^{14}N$ Nuclear Quadrupole Coupling Constants in the $\beta$-HMX Molecule**

| | $e^2qQ$ (MHz) | | | | |
|---|---|---|---|---|---|
| nucleus[a] | D95v | D95 | D95u[b] | 6-311g | exptl |
| 1, 2 | 1.347 | 1.352 | 1.442 | 1.433 | 0.840[c] |
| 7, 8 | 1.262 | 1.265 | 1.369 | 1.346 | 0.806[c] |
| 3, 4 | −5.925 | −5.928 | −5.936 | −5.953 | 5.791[d] |
| 5, 6 | −5.993 | −5.999 | −6.070 | −6.089 | 6.025[d] |

[a] The numbering for the different $^{14}N$ nuclei is as in Figure 1. [b] u refers to uncontracted basis set for carbon, nitrogen, and oxygen derived from D95 (ref 15). [c] Experimental results are from double-resonance measurements in ref 5 and refer only to the magnitude of $e^2qQ$. Also the assignments of the experimental $e^2qQ$ to the nuclei (N1,N2) and (N7,N8) are tentative and based on our theoretical results on $e^2qQ$ *and* $\eta$. [d] Experimental results are for a single crystal and taken from ref 4 and refer only to the magnitude of $e^2qQ$.

**TABLE 2: Asymmetry Parameters for $^{14}N$ Nuclei in the $\beta$-HMX Molecule**

| | $\eta$ | | | | |
|---|---|---|---|---|---|
| nucleus[a] | D95v | D95 | D95u[b] | 6-311g | exptl |
| 1, 2 | 0.784 | 0.785 | 0.553 | 0.565 | 0.42[c] |
| 7, 8 | 0.677 | 0.679 | 0.571 | 0.590 | 0.48[c] |
| 3, 4 | 0.458 | 0.458 | 0.432 | 0.438 | 0.4977[d] |
| 5, 6 | 0.517 | 0.516 | 0.490 | 0.497 | 0.5180[d] |

[a] The numbering for the different $^{14}N$ nuclei are as in Figure 1. [b] u refers to uncontracted basis set for carbon, nitrogen, and oxygen derived from D95 (ref 15). [c] Experimental results are from ref 5 and the assignments to nuclei (N1,N2) and (N7,N8) are tentative, based on the comparison between our theoretical values of $e^2qQ$ and $\eta$ and the experimental results for them. [d]Experimental results are for a single crystal and taken from ref 4.

the efg tensor from the nuclear charges in the molecule whereas the second term on the right represents the electronic contributions. The nuclear charge for the nucleus N is $\zeta_N$ and $R_{jN}$ and $R_{kN}$ are the components of the position vector $\mathbf{R}_N$ with $j$, $k = 1$, 2, 3 referring to $X$, $Y$, $Z$ Cartesian coordinates, the magnitude $R_N$ of $\mathbf{R}_N$ representing the distance of the nucleus N from the nucleus under study. In the second term on the right in eq 1, the summation over $\mu$ refers to the occupied orbitals, the factor 2 being applied to take care of the contributions from paired spin up and down states that involve the same molecular orbital wave function $\psi_\mu$. In the second term of eq 1, $r_j$ and $r_k$ represent Cartesian components of the position vector **r** for an electron with respect to the nucleus whose quadrupole interaction is under study, $r$ being the magnitude of this position vector. After obtaining the components $V_{jk}$ using the above formula, the calculated efg tensor is diagonalized to get its principal components $V_{j'j'}$. The coupling constants $e^2qQ$ to compare with results from experimental measurements are obtained using the nuclear quadrupole moment $Q$ and the largest principal component $V_{z'z'}$ of the efg tensor, the convention[3] for the principal axes X′, Y′, and Z′ being chosen such that $|V_{z'z'}| > |V_{y'y'}| > |V_{x'x'}|$. The asymmetry parameter $\eta$ is given by $(V_{x'x'} - V_{y'y'})/V_{z'z'}$. It is worthwhile to remark here that, since in our calculations we deal with all the electrons in the molecule in molecular orbital states, Sternheimer antishielding effects[17] are directly included,[18] obviating the need to incorporate them through Sternheimer antishielding parameters.

## III. Results and Discussion

Using the procedure just discussed, we have calculated the electronic wave functions for $\beta$-HMX and used them to obtain the efg tensors at the different nuclei. From the latter, one can evaluate[3] the nuclear quadrupole coupling constants $e^2qQ$ and asymmetry parameters $\eta$ for the nuclei, $^{14}N$, $^{17}O$, and $^2H$, that we have studied, the latter corresponding to deuterated $\beta$-HMX. The evaluation of the $e^2qQ$ requires a knowledge of nuclear quadrupole moments $Q$ for all the nuclei. For the nitrogen nucleus, we have made use of the value 0.015 barns (b) obtained through an accurate many-body calculation[19] in the ground state of nitrogen atom to derive $Q(^{14}N)$. For $^{17}O$ and $^2H$ we have used the values −0.025 78 and 0.002 86 b, respectively, from a recent tabulations[20] of nuclear quadrupole moments. The calculated coupling constants and asymmetry parameters in $\beta$-HMX are presented in Tables 1 and Table 2, respectively, along with the experimental results. The numbering of the various nitrogen nuclei in Tables 1 and 2 is taken from Figure 1. Experimental results for $e^2qQ$ and $\eta$ are currently available[4,5] for both the ring and peripheral $^{14}N$ nuclei. Although there are four $^{14}N$ nuclei in the ring, only two sets of nitrogen coupling constants and asymmetry parameters are observed[4] from nuclear quadrupole resonance experiments because, as discussed in section I, the four ring nitrogen nuclei can be grouped as two pairs of equivalent nuclei, namely the axial (N5,N6) and equatorial (N3,N4), because of the $C_2$ rotation symmetry[6] about the line N3−N4. The observed $e^2qQ$ and $\eta$ for the ring nuclei have been assigned[4] experimentally to the equatorial and axial $^{14}N$ nuclei using the nature of the temperature dependences of the corresponding resonance frequencies in nuclear quadrupole resonance. The four $^{14}N$ nuclei in the peripheral $NO_2$ groups also divide up into two pairs of equivalent nuclei (N1,N2) and (N7,N8), with the corresponding $e^2qQ$ and $\eta$ for them from our investigations being listed in Tables 1 and 2. Two sets of $e^2qQ$ and $\eta$ are observed[5] experimentally, but no assignment has been made with respect to the two pairs (N1,N2) and (N7,N8), unlike the case of ring $^{14}N$ nuclei, because comparable information on the temperature dependences of the NQR frequencies for the $NO_2$ groups is not currently available.

In analyzing the calculated and experimental $e^2qQ$ and $\eta$ for the $^{14}N$ nuclei, we analyze first the convergence of the results with respect to the size of the extensive variational basis sets chosen,[10] namely, D95v, D95, D95u, and 6-311g described in section II. The number of basis functions involved in these basis sets as described in section II increases continuously as one goes from D95v to 6-311g, increasing the variational flexibility of the basis sets. The calculated results for $e^2qQ$ and $\eta$ in Tables 1 and 2 for the ring and peripheral nitrogen nuclei respectively show very good convergence with respect to the sizes of the sets of basis functions, providing confidence in the calculated results. From Tables 1 and 2, one observes that the values of the nuclear quadrupole coupling constants for the equatorial and axial pairs within the ring are quite close to each other, differing by only about 0.13 MHz for the D95u case. A similar behavior is also observed for the peripheral nitrogens (N1,N2) and (N7,N8) on the $NO_2$ groups, which also divide into pairs because of the $C_2$ rotation symmetry about the line N3−N4. On the other hand, there is a strong difference in the values of $e^2qQ$ for the ring and peripheral nitrogens, the values for the latter being about a factor of 4 smaller than for the ring nitrogens.

It is instructive to try to understand physically the origin of the large difference in the coupling constants for the ring and peripheral $^{14}N$ nuclei in terms of the Townes and Dailey local approximation[21] considering the geometry around the two types of nitrogen atoms in $\beta$-HMX. Thus, considering the bonding situation at the peripheral nitrogens of the four $NO_2$ groups first, the environment of the nitrogen atom for any of these groups is planar, with the three neighbors, the two oxygens, and one ring nitrogen on the same plane as the nitrogen of the $NO_2$ group. This allows the latter nitrogen atom to form double bonds with the neighbors, more strongly with the two oxygens, because they have single unpaired $\pi$ electrons while the ring nitrogen has a pair of $\pi$ electrons. This double bonding leads to significant depletion in the population of the peripheral nitrogen atom orbital perpendicular to the plane of the neighbors from the two electrons in the lone pair, making the charge distributions around the $^{14}$N nucleus closer to cubic symmetry than if the lone pair was isolated and remained localized on the nitrogen atom. In the latter case, in terms of Townes and Dailey theory,[21] the field gradient would have originated from a single unbalanced p electron in the direction perpendicular to the plane, the depletion due to double-bond formation making the unbalanced p electron population substantially smaller than unity.

In the case of ring nitrogens, the three neighboring atoms, the peripheral nitrogen and two carbon neighbors, are not in a planar configuration, in contrast to the situation for the peripheral nitrogen. The bond angles subtended by the neighbors at the ring nitrogens are larger than 109° 28′ associated with tetrahedral bonding but smaller than 120° corresponding to the planar configuration. Considering the extreme case of the tetrahedral-type configuration, the bonding to neighboring atoms, as in the methane molecule, would be expected to be primarily single bond in nature involving one $\sigma$-electron on the carbon atom per bond. Of the five electrons in the ring nitrogen atom, three are single bonded to three neighbors and two others are directed in the fourth tetrahedral direction (where there is no neighbor to bond with) as a lone pair. If there were four electrons per atom as in carbon, then tetrahedral bonding as in methane would lead to zero-field gradient. Having one more electron as a part of a lone pair on the ring nitrogen would lead to a field gradient associated with this extra electron. This is unlike the situation in the planar bonding case as for the peripheral nitrogen where double bonding to oxygens in the $NO_2$ group, and to a lesser extent to the neighboring peripheral nitrogen, lead to a substantial reduction in the field gradient from that due to a single "unbalanced" electron in the Townes and Dailey sense. As mentioned earlier, the configuration for the ring nitrogen is not exactly tetrahedral but intermediate between tetrahedral and planar. One would therefore expect the field gradient for the ring $^{14}$N to be smaller than in the extreme tetrahedral bonding case with a lone pair of electrons, but significantly larger than for the $^{14}$N nucleus on the peripheral nitrogen associated with the planar configuration in $NO_2$ as found theoretically from our calculation (Tables 1 and 2).

It is interesting to speculate about the net charges expected on the ring and peripheral nitrogen atoms on the basis of the bonding to neighbors, which explains physically the trend of the efg's between the peripheral and ring nitrogen nuclei. The larger localized electron population expected at the ring nitrogens from the discussion in the preceding paragraph suggests that these nitrogens would be negatively charged relative to the peripheral nitrogens. We have tabulated in Table 3 the effective charges on all the atoms in $\beta$-HMX using our calculated electronic wave functions and the Mulliken approximation. The calculated effective charges on the peripheral nitrogens are found to be positive while the ring nitrogens carry negative charges. The trend is thus in keeping with physical expectations and provides a linkage between the $e^2qQ$ for $^{14}$N nuclei and effective charges on the corresponding atoms. It is hoped that the charges listed in Table 3 will be helpful in understanding the strength and possibility of attachment of different molecular groups at the various atomic sites in this energetically important molecule.

It is worthwhile to note from Table 2 that the calculated asymmetry parameters $\eta$ for the ring and peripheral $^{14}$N nuclei are of comparable magnitudes (with the values of $\eta$ for the peripheral nuclei a little higher than for the ring nuclei) although the quadrupole coupling constants are so different. This difference in behavior of $e^2qQ$ and $\eta$ is not surprising considering the fact that the former is dependent primarily on the departure of the charge distribution from spherical and cubic symmetry while $\eta$ is dependent on the departure from axial symmetry. It is unfortunately not possible to explain from relatively simple physical considerations, as was the case for $e^2qQ$, the expected variations in the asymmetry parameters for the two types of $^{14}$N nuclei. It is also interesting to note that both the calculated values of $e^2qQ$ and $\eta$ individually as well as their trends in going from ring to peripheral nitrogens are comparable for RDX[10] and $\beta$-HMX. This is not unexpected because the environments and nature of bonding of the nitrogen atoms in both molecules resemble each other.

**TABLE 3: Predicted Charges on Different Nuclei in $\beta$-HMX**

| index | nuclei | atomic charge |
|---|---|---|
| 1, 2 | N | 0.444 |
| 3, 4 | N | −0.238 |
| 5, 6 | N | −0.339 |
| 7, 8 | N | 0.428 |
| 9, 10 | O | −0.322 |
| 11, 12 | O | −0.316 |
| 13, 14 | O | −0.303 |
| 15, 16 | O | −0.288 |
| 17, 18 | C | −0.142 |
| 19, 20 | C | −0.046 |
| 21, 22 | H | 0.250 |
| 23, 24 | H | 0.323 |
| 25, 26 | H | 0.297 |
| 27, 28 | H | 0.251 |

We turn next to the nature of agreement between theory and experiment[4] for the coupling constants $e^2qQ$ and $\eta$ for the ring $^{14}$N nuclei. From Tables 1 and 2, it appears that there is good agreement between the magnitudes of $e^2qQ$ from experiment (since as remarked earlier, the signs of $e^2qQ$ cannot be obtained from NQR measurements) and theory and between the theoretical and experimentally observed values of $\eta$. For the rest of the paper, we shall use the results obtained for the choice of D95u basis set in Tables 1 and 2 as the theoretical results to compare with experiment as we had done[10] for RDX. As a consequence of this good agreement, one is also able to explain the trends in both $e^2qQ$ and $\eta$ from experiment, namely, that of slightly higher values for the magnitudes of $e^2qQ$ and values of $\eta$ for the axial nitrogens (N5,N6) on the ring as compared to that for the equatorial (N3,N4) ones. The quantitative difference between $e^2qQ$ for the axial and equatorial $^{14}$N nuclei, however, seems from Table 1 to be a bit smaller for the theoretical predictions as compared to experiment, while from Table 2 the reverse is the case for $\eta$. These small but significant differences between theory and experiment could well be the result of slight uncertainties, within experimental error, in the structural data for the relative positions[6] of the nearest neighbor nitrogen, carbon, and oxygen atoms for both the equatorial and axial nitrogens. It is also possible that incorporation of many-body effects,[22] somewhat difficult to do for such a large molecule, could explain the small differences between theory and experiment (Tables 1 and 2). It would also be useful to examine the possible influence of intermolecular bonding with atoms of neighboring molecules as was suggested in our earlier work[10] on the RDX system. The bond distances between neighboring atoms[4] in neighboring molecules of $\beta$-HMX are in general somewhat smaller than for[9] RDX, suggesting somewhat stronger intermolecular effects that are also indicated by the weaker temperature dependence[4] of ring $^{14}$N NQR frequencies as compared to those[9] in RDX. In general, however, the overall good agreements between theory (ref 10 and the present work) and experiment[4,9] for both RDX and $\beta$-HMX molecules suggest that the electron distributions in the neighborhood of the ring nitrogen atoms and, by inference, over the entire ring, are well described by Hartree−Fock calculations carried out on the isolated molecule in the present work on $\beta$-HMX and our earlier work[10] on RDX. The agreement between theory and experiment for the ring $^{14}$N nuclei is somewhat more definitive in the present work on $\beta$-HMX because of the fact that the assignments of the experimental $e^2qQ$ and $\eta$ have been made more unequivocally[4] from temperature dependence data for the NQR frequencies than in the case of[9] RDX.

Further insights into the influence of intermolecular bonding effects is obtained in comparing the calculated $^{14}$N nuclear quadrupole interaction parameters for the peripheral $NO_2$ groups with experiment. From Table 1, the values of $e^2qQ$ for the two pairs of equivalent nuclei are considerably smaller, by about a factor of 4, than for the ring $^{14}$N as discussed earlier in this section. This makes the expected values of NQR frequencies rather small, namely, 1.28 and 0.88 MHz for (N1,N2) and 1.22 and 0.83 MHz for (N7,N8), which are obtained using the calculated $e^2qQ$ and $\eta$ in Tables 1 and 2 and the expressions for the two frequencies, $\nu_+$ and $\nu_-$, for spin 1 nuclei available in the literature.[3] This makes their detection by direct NQR spectroscopy difficult, since the signals are expected to be weak for low frequencies. However, one can detect weak NQR signals by double-resonance techniques.[7,8] This basically involves studying the changes in strengths of stronger NMR or NQR signals of other nuclei in the system as one applies varying frequencies to the nuclei with weaker resonances. At the resonance frequencies for the latter nuclei, their dipole−dipole interactions with the stronger resonance nuclei is averaged out and leads to changes in their line widths (and hence relaxation rates) and consequent changes in the strength of their NMR or NQR signals. A method[7] based on such techniques[8] has been recently used to obtain the experimental[5] values of two sets of frequencies, namely (0.72, 0.54) and (0.72, 0.49) MHz. These frequencies lead to two sets of $e^2qQ$ and $\eta$, namely (0.840 MHz, 0.42) and (0.806 MHz, 0.48) mentioned in Section I. However no assignments have been made experimentally for these to the two pairs of peripheral $^{14}$N nuclei, namely (N1,N2) and (N7,N8). On comparing the experimental[5] and theoretical values in Tables 1 and 2, it appears that the experimental values for $e^2qQ$ are about 40% smaller than theory and those for $\eta$ about 20% smaller than theory, in contrast to the much closer agreement found for the ring $^{14}$N nuclei. The main source for the difference that suggests itself is the influence of intermolecular bonding effects.

The intermolecular bond distances between the oxygen, nitrogen, and carbon atoms in adjacent molecules are all larger than the corresponding van der Waals distances. The same is true for the intermolecular bond distances between the nitrogen (both ring and peripheral) of a $\beta$-HMX molecule and the hydrogen atoms in neighboring molecules that are attached to the carbon atoms. The major and important exception is the case of oxygen atoms next to the peripheral nitrogens in the $NO_2$ groups and hydrogen atoms in neighboring molecules, which are all less than the van der Waals distances of 2.60 Å. In particular, the shortest such O−H distance, between the atom O(11) and H(27) in a neighboring molecule, is only 2.36 Å. One thus expects significant distortion in the electron density around the oxygen atoms of the $NO_2$ groups through both the van der Waals interactions between the oxygen and corresponding hydrogen atoms of the adjacent molecules as well as through covalent bonding effects between these atoms. The changes in electron density on the oxygen atoms are expected to influence the electron density distributions around the nitrogen atoms of the $NO_2$ groups through the changes in the $\sigma$ and $\pi$ bonding between the nitrogen and oxygen atoms. There will of course be some direct influence of the van der Waals interaction between the nitrogen atoms of the $NO_2$ groups and atoms of the neighboring molecules in changing the electron distribution on the nitrogen atoms in the $NO_2$ groups. This is, however, expected to be less important than the influence of changes through the strong covalent interactions between the nitrogen and oxygen atoms of the $NO_2$ groups, brought about by the changes in the electron densities on the oxygens through intermolecular interactions between the latter and hydrogen atoms in the neighboring molecules. These changes in the electron distributions on the peripheral oxygen and nitrogen atoms are expected to be much more significant compared to corresponding changes on the ring nitrogen and carbon atoms of the $\beta$-HMX molecule. The changes in electron distributions around the peripheral nitrogen nuclei induced through the changes in the electron density at oxygens of the $NO_2$ groups can in principle lead to differences of the type observed between our theoretical values of $e^2qQ$ and $\eta$ in Tables 1 and 2 and the experimental values for the $^{14}$N nuclei. For the ring nitrogen nuclei, the direct influence of the interactions between the corresponding nitrogen atoms and atoms in neighboring molecule is expected to be weak as in the case of the peripheral nitrogen atoms. Further, the influence on the ring nitrogen atoms of the electron density changes on the oxygen atoms of the $NO_2$ groups due to their intermolecular interactions is also expected to be relatively weak due to the fact that changes in covalent bonding effects for the ring nitrogen atoms can occur only indirectly through the peripheral nitrogen atoms that are directly bonded to the oxygen atoms of the $NO_2$ group. This reasoning could explain the substantially better agreement between the calculated (for the free $\beta$-HMX molecule) and measured values of $e^2qQ$ for the ring $^{14}$N nuclei as compared to the peripheral $^{14}$N nuclei and also the situation in the case of $\eta$.

There is one other source that could contribute bridging the gap between theory and experiment for $e^2qQ$ and $\eta$ for the peripheral $^{14}$N nuclei. This is the role of many-body effects,[22] which has not been considered for both the ring and peripheral $^{14}$N nuclei. As has been shown extensively through first-principle accurate many-body perturbation theoretic calculations in atomic systems[22−24] on hyperfine interaction properties including nuclear quadrupole interaction effects and other wavefunction dependent properties, many-body correlation effects are expected to be more important when the system concerned is more deformable. This deformability, which governs the strength of the perturbation produced by the difference between the actual and Hartree−Fock Hamiltonians, leads to stronger excitations to higher states in perturbation theory and hence greater impact on observable properties. Since the $NO_2$ group involves both the $\sigma$ and $\pi$ bonding between nitrogen and oxygen with the latter being usually weaker, one expects stronger many-body effects than for the ring nitrogen where the nitrogen is primarily $\sigma$ bonded to its neighbors. However, a quantitative treatment of many-body effects by either perturbation theory or configuration interaction techniques is expected to be very time-consuming for a large molecule like $\beta$-HMX. Additionally, it has been shown in atomic many-body perturbation theoretic investigations[23,24] that the convergence in perturbation investigations with respect to the number of excited states used is sensitive to the choice of potentials used in the zero-order one-electron theory calculations that serve as the starting point for

**TABLE 4: Theoretical Values of Nuclear Quadrupole Coupling Constants and Asymmetry Parameters for $^{17}$O Nuclei in $\beta$-HMX**

| nuclei | $e^2qQ$ (MHz)[a] | $\eta$[a] |
|---|---|---|
| 9, 10 | −16.192 | 0.985 |
| 11, 12 | −16.159 | 0.907 |
| 13, 14 | −16.046 | 0.872 |
| 15, 16 | −16.004 | 0.849 |

[a] Based on efg tensors obtained using the D95u basis set (ref 15).

**TABLE 5: Theoretical Nuclear Quadrupole Coupling Constants and Asymmetry Parameters for $^2$H in $\beta$-HMX**

| nuclei | $e^2qQ$ (MHz)[a] | $\eta$[a] |
|---|---|---|
| 21, 22 | 0.192 | 0.071 |
| 23, 24 | 0.204 | 0.072 |
| 25, 26 | 0.197 | 0.105 |
| 27, 28 | 0.208 | 0.071 |

[a] Based on efg tensors obtained using the D95u basis set (ref 15).

many-body perturbation and configuration interaction investigations. The convergence is greater when one uses the physical $V^{N-1}$ potentials[23] for generating excited states rather than the $V^N$ or Hartree−Fock potential used for the ground many-electron state of the atomic or molecular system. In the former case, for neutral systems there are bound excited states in addition to continum positive energy states available to use in perturbation theory or configuration interaction treatment, while for $V^N$, there are only continuum states available. Unfortunately, in currently available computer programs, only the $V^N$ type excited states are available, which are expected to be reasonably adequate for correlation energy calculations but not for correlation effects on properties dependent on electronic wave functions, like nuclear quadrupole and magnetic hyperfine interactions. It is hoped, however, that $V^{N-1}$ programs will be developed in the future for treatment of many-body effects on molecular properties.

It is thus clear that one needs to deal with both many-body effects as well as the influence of intermolecular interactions to try to understand the difference between experiment and theory for peripheral $^{14}$N, in contrast to the case of ring $^{14}$N nuclei. It is our feeling that intermolecular interactions would be more important in effect, mainly because the oxygens of the $NO_2$ groups are quite close to the hydrogen atoms of neighboring molecules, but the complete answer will be available only when both effects are quantitatively treated, which we hope will be done in the future. It is interesting to note that from Tables 1 and 2 the calculated value of $\eta$ is smaller for the peripheral nitrogen nuclei (N1,N2) than (N7,N8), while the reverse is true for $e^2qQ$, in keeping with experimental trends for the two observed resonances for $^{14}$N nuclei in the $NO_2$ group. One might then associate the higher observed $e^2qQ$ to the nuclei (N1,N2) and the lower one to (N7,N8), but the final assignment will depend upon the results from calculations of intermolecular and many-body effects. Lastly, since the peripheral $^{14}$N quadrupole interactions are rather small and consequently the associated NQR frequencies are difficult to detect, they have been measured by special double-resonance techniques.[5,7] In view of the importance of the values of these frequencies, and correspondingly $e^2qQ$ and $\eta$, in providing valuable information about the electronic structure of the $NO_2$ groups in $\beta$-HMX and on intermolecular bonding, it would be helpful to have additional measurements to confirm the measured frequencies from the published results[5] that have been used here for comparison with theory.

In Tables 4 and 5 we have tabulated the values of $e^2qQ$ and $\eta$ for the $^{17}$O and $^2$H (deuteron) nuclei, calculated using the Hartree−Fock wave functions for the $\beta$-HMX molecule in the present work, using the values of the corresponding available quadrupole moments mentioned earlier in this section. The $^{17}$O nuclei are considered to replace the abundant $^{16}$O nuclei in the $NO_2$ groups while the deuteron nuclei replace the protons attached to the $CH_2$ groups in Figure 1. The $^{17}$O and $^2$H nuclei, like the $^{14}$N nuclei in Tables 1 and 2, separate into pairs because of the $C_2$-type rotational symmetry about the line joining N3 and N4, the equatorial nitrogens. The values of $e^2qQ$ and $\eta$ for all four pairs of $^{17}$O nuclei are seen from Tables 4 and 5 to be quite close to each other as are those for the $^2$H. There are, however, some interesting small but significant differences in $\eta$ for the $^{17}$O nuclei such as those between the pairs (9,10) and (11,12) on one hand and (13,14) and (15,16) on the other nuclei. Similar significant differences in $\eta$ for $^2$H nuclei are found between the three pairs (21,22), (23,24), and (27,28) on one hand and (25,26) on the other. It will be very helpful in the future to have experimental data for $e^2qQ$ and $\eta$ for these $^{17}$O and $^2$H nuclei to compare both quantitatively with our theoretical results in Tables 4 and 5 for the free $\beta$-HMX molecule and with the trends seen from the latter. The quantitative comparison between theory and experiment is also expected to be particularly important. This will allow us to see if the substantial intermolecular interactions between oxygen and hydrogen atoms, which are suggested to lead to the significant observed reductions of $e^2qQ$ and $\eta$ for peripheral $^{14}$N nuclei in $\beta$-HMX as compared to the calculated theoretical values for the free molecule, also influence the $^{17}$O and $^2$H results in a similar manner. It is hoped that the measurements of $e^2qQ$ and $\eta$ can be carried out through double-resonance techniques[7,8] because of the expected weakness of the signals for these nuclei in standard NQR measurements both due to weak abundance of these nuclei and in the case of $^2$H, due to the small size of the quadrupole coupling constants. Alternatively, one could also use NMR techniques[11] using enriched systems with greater concentrations of $^2$H and $^{17}$O nuclei and higher magnetic fields to enhance the sensitivity (signal to noise ratio).

## IV. Conclusion

The electronic structure of the $\beta$-HMX molecule has been studied in this work by the Hartree−Fock procedure. Using the calculated wave functions, we have studied the nuclear quadrupole interactions for $^{14}$N, $^{17}$O, and $^2$H in this molecule. The quadrupole coupling constants and asymmetry parameters for the $^{14}$N nuclei in the ring are found to be in good agreement with experimental results.[4] There are, however, some small but significant differences between $e^2qQ$ and $\eta$ between the predicted and experimental values of the differences between the equatorial and polar $^{14}$N nuclei that need to be explained, and possible factors for bridging these differences are discussed, including the role of intermolecular bonding between neighboring molecules in the solid. The peripheral $^{14}$N nuclear quadrupole coupling constants are calculated to be substantially smaller, (less than a factor of 4) than the ring $^{14}$N quadrupole coupling constants, the smallness being verified by recent double-resonance measurements[5] in $\beta$-HMX. However, the magnitudes of the measured quadrupole coupling constants and asymmetry parameters $\eta$ for the two sets of equivalent pairs of nitrogen atoms in the molecule are found to be about 40% and 20%, respectively, smaller than the calculated values for an isolated $\beta$-HMX molecule. A suggested source for the difference between experiment and theory that should be examined is the influence of intermolecular bonding effects involving the oxygen atoms of the $NO_2$ groups and hydrogen atom ligands of carbons on neighboring molecules. The influence of the intermolecular effect on oxygens is communicated through their bonding to the nitrogen atoms of the $NO_2$. The possible role of many-body effects is also suggested as a candidate to be examined for improving the agreement between theoretical and experimental values of $e^2qQ$ and $\eta$ for $^{14}N$ nuclei of the $NO_2$ groups. In view of the fact that the comparison between theory and experiment for the $^{14}N$ nuclear quadrupole interactions in $NO_2$ groups provides an index of the importance of intermolecular bonding effects and the fact that the peripheral $^{14}N$ frequencies are difficult to measure due to their small sizes, we feel that it would be important to have additional measurements of these frequencies to confirm the results obtained by a single measurement[5] so far. Reasons are suggested for both intermolecular bonding and many-body effects being relatively small for the ring $^{14}N$ nuclear quadrupole interaction and therefore not influencing significantly their good agreement with experiment. There is a need for experimental data on the nuclear quadrupole interactions for $^{17}O$ and deuteron nuclei to compare with the theoretical predictions in our present work. In particular, it would be interesting to see if the comparison between experimental quadrupole interaction parameters for $^{17}O$ and deuterons and our theoretical predictions for the free $\beta$-HMX molecule suggests significant influence of intermolecular bonding effects since the oxygen and hydrogen atoms of neighboring molecules have smaller separations than the sums of their van der Waals radii. Conclusions about the importance of intermolecular bonding of oxygen and hydrogen atoms are also important since these intermolecular interactions have been invoked in this work to explain the observed differences between the theoretical $^{14}N$ nuclear quadrupole interaction parameters for the peripheral nitrogen atoms and their observed values.[5] However, the overall quantitative agreement obtained between theory and experiment[4] for the ring $^{14}N$ nuclei in $\beta$-HMX from the present investigation and in RDX[9] from our earlier work[10] suggests that the Hartree–Fock procedure leads to a good understanding of the electron distributions in energetic molecules. This observation is indirectly complemented by the fact that while there are some differences between the predicted and measured $e^2qQ$ and $\eta$ for the peripheral $^{14}N$ nuclei, plausible reasons, which need to be verified, are suggested for explaining the differences between theory for the free molecule and experimental results in the solid state, particularly intermolecular bonding effects. In view of this, there is reason for encouragement to proceed in the future to the more complicated problem of trying to understand quantitatively the observed temperature dependence of $e^2qQ$ and $\eta$ for the ring $^{14}N$ nuclei in both $\beta$-HMX[4] and RDX.[9] This would require an understanding of the natures of motional effects both within the molecules and with respect to neighboring molecules, the latter involving intermolecular interactions between neighboring molecules.

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