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Theory of Electronic Structure and Nuclear Quadrupole Interactions in Heroin

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A first principle investigation has been carried out for the electric field gradient tensor at the ^{14}N nucleus in heroin ($C_{21}H_{23}NO_5$) using the Hartree−Fock−Roothaan procedure for determination of the electronic structure employing atomic coordinates based on available X-ray diffraction data. The hydrogen positions were not available from experiment and were determined by energy optimization in our investigations. Our calculated quadrupole coupling constant e^2qQ for ^{14}N was found to be −4.906 MHz, the magnitude being in good agreement with the corresponding recently available magnitude of 5.3163 MHz from nuclear quadrupole resonance measurements. The value of the asymmetry parameter η was found to be 0.054, the smallness of its size being in agreement with that of the experimental value of 0.028. Possible sources that could further improve the quantitative agreement between theory and experiment are discussed. The quadrupole interaction parameters for the ^{17}O and ^{2}H nuclei are presented with the hope that experimental values for them will become available in the future, which would allow a comprehensive comparison between theory and experiment for all the nuclei in heroin, enabling a thorough test of the calculated electron distribution in the molecule.

I. Introduction

In recent years, there is considerable effort being made to use ^{14}N as a sensor[1,2] for the detection of controlled substances using pure nuclear quadrupole resonance (NQR)[3] spectroscopy. Since the frequencies of the NQR signals associated with the various nuclei depend upon the nuclear quadrupole interaction (NQI) parameters,[3] namely, the quadrupole coupling constant e^2qQ and asymmetry parameter η, which in turn depend sensitively on the electron distribution in the vicinity of the nucleus of interest, the quantitative understanding of the origin of the NQI parameters from first-principle quantum mechanical investigations is of great interest. In the present paper we have investigated the electronic structure of heroin free base (diacetylmorphine, $C_{21}H_{23}NO_5$) for which the experimental nuclear quadrupole interaction parameters for the ^{14}N nucleus have recently become available.[4]

In the heroin molecule only one nitrogen site is found from crystallographic data, and as expected, only one set of nuclear quadrupole interaction parameters, e^2qQ and η, have been observed experimentally[4] by NQR spectroscopy in polycrystalline samples. In the present paper our aim is to explain these observed parameters, based on a first-principle quantum mechanical study of the electronic structure. The method adopted for the present study is based on the Hartree−Fock−Roothaan variational procedure[5] using Gaussian basis functions[6] on the different atoms in the molecule. This procedure has been tested successfully[7] by our group and others for the investigation of localized properties including nuclear quadrupole and magnetic hyperfine interactions in a number of molecular and solid state systems.

In section II, we have presented briefly the procedure used for this calculation. Following this, in section III, we present our results from this investigation and discussions. Section IV summarizes our main conclusions from this study with suggestions for future work.

II. Procedure

As in previous investigations[8−10] on energetically and physiologically important molecules, we have made use of the Hartree−Fock−Roothaan variational procedure for closed-shell systems for our quantum-mechanical investigation of the electronic structure of heroin, since it involves an even number of electrons with zero total spin. This method is very well documented in the literature[5,7] and hence will not be described here. We have employed a linear combination of Gaussian basis functions[11] as trial wave functions in our variational calculation because of the economy they provide in terms of computational effort in evaluating the multicenter integrals in molecular problems. The set of programs[6] referred to as Gaussian 92 has been used for the present investigation. The choices of Gaussian basis sets used in our work are discussed later in this section.

The atomic arrangement for heroin is shown in Figure 1, which consists of 50 atoms and 196 electrons. All the atomic positions in this molecule except those of the hydrogens are obtained from X-ray diffraction measurements.[12] There are no experimental data available for the hydrogen positions. Hence we have obtained these positions by minimizing the total Hartree−Fock energy with respect to them, our results being presented in Table 1.

From Figure 1 one can see that all the hydrogens are bonded to carbon atoms. The bond distances of these hydrogens with

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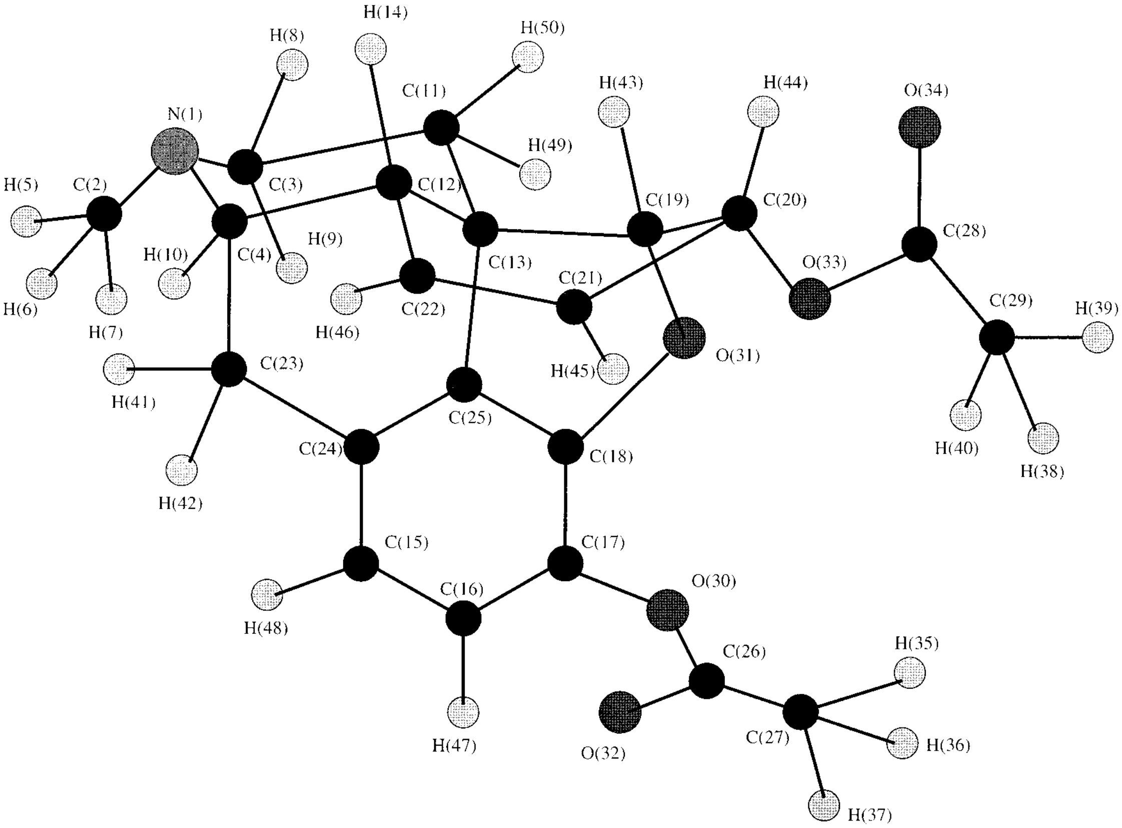

Figure 1. Atomic arrangement in heroin ($C_{21}H_{23}NO_5$). The arrangement is based on the atomic coordinates of C, N, and O atoms from X-ray diffraction data in ref 12 and H-atom positions determined by energy optimization in this work.

TABLE 1: Results for Hydrogen Positions Obtained through All-Electron Energy Optimization in Heroin (Basis Set STO-3G)

nuclei	*X*	*Y*	*Z*	C−H (Å)
H(5)	2.433	0.585	15.052	1.09
H(6)	1.178	1.754	14.612	1.09
H(7)	2.182	1.006	13.366	1.09
H(8)	4.674	1.122	14.846	1.09
H(9)	4.538	1.687	13.193	1.09
H(10)	1.805	3.967	14.242	1.09
H(14)	3.719	4.783	15.451	1.09
H(35)	9.872	6.646	9.666	1.09
H(36)	10.290	5.429	8.458	1.08
H(37)	9.035	6.629	8.118	1.09
H(38)	8.149	9.627	12.486	1.09
H(39)	9.642	8.868	13.014	1.09
H(40)	8.619	8.063	11.821	1.09
H(41)	2.956	2.574	12.193	1.10
H(42)	1.769	3.661	11.795	1.08
H(43)	6.948	5.243	14.886	1.09
H(44)	5.860	7.179	15.206	1.10
H(45)	4.079	8.109	13.468	1.08
H(46)	2.369	6.434	13.731	1.08
H(47)	5.446	4.615	8.633	1.08
H(48)	3.334	3.699	9.617	1.08
H(49)	6.493	2.743	14.123	1.09
H(50)	5.654	3.200	15.600	1.09

respect to their nearest-neighbor carbon atoms are given in the last column of Table 1 and are all found to lie between 1.08 and 1.10 Å as is usual in organic molecules, providing confidence about the hydrogen positions determined from first-principles theory. These hydrogen positions together with the positions of other atoms from X-ray diffraction measurements have been utilized for our electronic structure investigations. The calculated electronic wave functions for the molecule were used for the evaluation of the NQI parameters (e^2qQ and η) at the ^{14}N nucleus. The evaluation of e^2qQ requires a knowledge of Q, the nuclear quadrupole moment, and for q and η one needs the principal components of the field gradient tensor. For $Q(^{14}N)$, we have used the value 0.015 barn as in our earlier work.[8−10] This value of $Q(^{14}N)$ is taken from an accurate relativistic many-body calculation[13] of the electric field gradient (efg) in the ground state of nitrogen atom for which the experimental value of e^2qQ was available. For the efg tensor components at the nucleus of interest, we have made use of the following expressions:[3]

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

where the first term on the right-hand side of eq 1 represents the contribution to the efg tensor components from the nuclear charges in the molecule, whereas the second term on the right represents the contribution from the electrons. The nuclear charge for the nucleus N is ζ_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 μ refers to the occupied orbitals, the factor 2 being applied to take care of the contributions from paired spin-up and spin-down states which involve the same molecular orbital wave function ψ_μ for a closed-shell system. In the second term of eq 1, r_j and r_k represent the components of the position vector $\mathbf{r}$ 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[3] in the principal axes system to get its principal components $V_{j'j'}$. The usual convention[3] for choosing the principal axes X', Y', and Z' is used, namely, $|V_{z'z'}| > |V_{y'y'}| > |V_{x'x'}|$. The parameter q in e^2qQ is given by the principal component $V_{z'z'}$ and the asymmetry parameter η is given by $(V_{x'x'} - V_{y'y'})/V_{z'z'}$. It should be remarked here that since this is an all-electron calculation involving both core and valence electrons of all the atoms, Sternheimer shielding or antishielding effects[14] are directly included, obviating the need to incorporate them through Sternheimer shielding or antishielding parameters estimated from results for them for free atoms and ions.

Next, turning to the choice of basis functions employed to obtain the molecular orbital wave functions that were used to evaluate the efg tensor components, we have carried out our investigations using STO-3G as well as two much more flexible basis sets D95 and D95U, which were utilized in our earlier investigations[8−10] on RDX, β-HMX, and cocaine. The last named basis set (D95U) involves uncontraction[8] of the outermost p-orbitals for C, N, O in the D95 basis set. The reason for uncontracting the p-orbitals is that they are expected[3] to make the most contributions to the field gradient tensor components. We have not made use of even more extensive basis functions like 6-311G because of the large amount of time that would be needed for this large molecule. However, from our experience[9,10] in RDX and β-HMX we do not expect the results to change significantly from D95U to 6-311G. To give an idea about the sizes of the basis sets utilized in this work on heroin involving 196 electrons, STO-3G involves 158 basis functions and 474 primitive Gaussians, whereas D95 involves 316 basis functions, twice as big as STO-3G, and 740 primitive Gaussians. The D95U choice involves 397 basis functions and 740 primitive Gaussians.

For the evaluation of the hydrogen coordinates in Table 1 by energy optimization, the time involved is rather large compared to that for obtaining electronic wave functions using known atomic coordinates. We have therefore used only the basis set referred to as STO-3G for determining the coordinates of the hydrogen atoms. Although the STO-3G basis set does not have as much flexibility as the more extensive basis sets D95 and D95U, it can provide a reasonably accurate description of the geometry of the molecules involving light atoms like C, N, O, H, while greatly reducing the computational effort, as has been seen in earlier investigations[10] in cocaine and fullerene[15] (C_{60}). Thus, in our earlier work on cocaine it has been observed that the hydrogen positions obtained by minimization of the total Hartree−Fock energy using STO-3G basis functions differ by less than 1% from the hydrogen positions obtained[16] by combining the X-ray diffraction data with three-dimensional Patterson analysis. Also in C_{60}, it has been seen[15] that the STO-3G basis set led to C−C bond distances within 1−2% of experimental results.

III. Results and Discussion

Using the procedure outlined in the preceding section, we have obtained the wave functions and the efg tensor components from which the nuclear quadrupole interaction parameters e^2qQ and η are calculated. The values of e^2qQ and η for ^{14}N nucleus for the different choices of basis functions used, and recently available experimental results for them, are listed in Table 2.

TABLE 2: ^{14}N Nuclear Quadrupole Coupling Constant and Asymmetry Parameter in Heroin

basis set	e^2qQ (MHz)[a]	e^2qQ (MHz)[b]	η	η[a]
STO-3G	−5.708	5.3163	0.030	0.0280
D95	−4.863		0.057	
D95U	−4.906		0.054	

[a] Theoretical results (this work). [b] Experimental results quoted are from NQR measurements;[4] only the magnitude of e^2qQ being available from these measurements.

The theoretical results for e^2qQ and η show good convergence in going from the basis set D95 to the more flexible set D95U. However, there is a significant difference between the results for these two basis sets and those with the minimal basis set STO-3G. This difference is not unexpected since the efg tensor is very sensitive to the anisotropy of the electron distribution near the nucleus of interest, and the anisotropy is expected to change in going from the minimal basis set STO-3G to the more flexible basis sets D95 and D95U. It is interesting to note from Table 2 that while the results with D95 and D95U are quite close to the experimental results, the STO-3G result for e^2qQ is equally close but higher in magnitude than experiment, the results with the other two choices being lower. The value of η for the STO-3G case however appears to be closer to experiment than for D95 and D95U. Thus, the STO-3G results overall appear to be closer to experiment than those for the D95 and D95U choices. However, the latter two basis sets are much more flexible than STO-3G as is also evidenced by the much lower total energies −1236.95 and −1237.01 hartrees for D95 and D95U, as compared to −1221.87 hartrees for the STO-3G basis set. Additionally, we have also found that in our recent investigations on RDX, β-HMX, and cocaine free base, the results for the nuclear quadrupole interaction parameters for the D95 and D95U basis sets are in significantly better agreement with experiment than for STO-3G. The reason for the expected better agreement for energy and properties dependent on energy (like bond distances) as compared to efg parameters for the STO-3G choice, which does not allow for as much flexibility in the variational procedure as other more extensive basis sets, is that energy involves an average over all regions of the molecule, while efg and other hyperfine properties are strongly dependent on restricted regions near the nucleus. From these considerations, one can consider the better agreement for η for STO-3G in Table 2 with experiment to be accidental and consider the results for D95 and D95U basis sets to be more representative of theory. In the discussions that follow, we shall therefore discuss the nature of the agreement with experiment for only the former two, and possible sources that could improve the agreement.

The theoretical result for the D95U basis set for the coupling constant e^2qQ is only about 7.5% smaller than experiment. The asymmetry parameters for both experiment and theory are both seen from Table 2 to be rather small, namely, 0.03 and 0.054, respectively. The quantitative difference between the theoretical and experimental η is not too significant because of their very small values, and the greater percentage difference in η as compared to e^2qQ is understandable because of the fact that the former involves the difference between $V_{x'x'}$ and $V_{y'y'}$, while e^2qQ involves only the single principal component $V_{z'z'}$.

To bridge the small but significant differences between theoretical and experimental results for e^2qQ and η, there are a number of sources that one could consider. One of these is the possibility that there is some inaccuracy in the atomic positions employed in the calculation of the electronic wave functions used for obtaining the efg tensor components. The atomic positions for carbon, oxygen, and nitrogen, especially the latter, obtained from X-ray structural data,[12] could have a significant range of error and the anisotropy of the electron distribution, on which the components of the efg tensor depend sensitively, could be affected by uncertainties in these positions. Correspondingly, the hydrogen atom positions determined here by energy optimization, especially those for H(5) through H(10) in Figure 1, bonded to the carbon atoms C(2), C(3), and C(4), which in turn are nearest neighbors of nitrogen atom, could have possible ranges of error that could influence the electron distribution and hence the components of the efg tensor for the ^{14}N nucleus. For testing this point, it would be helpful to have a determination of the H atom positions by neutron diffraction measurements[17] on the deuterated compounds, as in RDX or β-HMX, to verify our calculated positions for the H atoms (Table 1). Additionally, it would be helpful to have a revised X-ray structure determination to test the available C, N, and O atom positions as well as information on the H-atom positions by Patterson synthesis, as in cocaine, to compare with our results for the H-atom positions (Table 1). A second source that could bridge the small differences between theoretical and experimental NQI parameters is the possibility of intermolecular interactions, especially between the nitrogen atom (and other atoms bonded to it) and atoms in neighboring molecules, which has been suggested from our earlier work[9] on β-HMX to influence the anisotropy of the electron density distribution around the ^{14}N nuclei in the latter system. The influence of intermolecular interactions would be somewhat time-consuming to test but would be desirable to carry out in the future. Further, as pointed out in our recent investigations on ^{14}N quadrupole interactions in other molecules of comparable size (RDX, β-HMX, and cocaine), the influence of many-body effects is difficult to test for large molecules of these types, from considerations of computational effort involved, but would be useful to study in the future. Lastly, the experimental results used in Table 2 for comparison with our calculated ^{14}N quadrupole interaction parameters are based on NQR measurements[4] for a sample of 97.9% purity. Since there could be some influence of impurities on the ^{14}N NQR frequencies, it would be very helpful, for quantitative comparison with our theoretical results, to have results for purer samples in the future.

It is important to emphasize that while the need for the improvements in theoretical and experimental investigations discussed here is important to attempt near-exact agreement between theory and experiment, our results and currently available experimental data are in better than 10% agreement for e^2qQ and the sizes of η from experiment and theory are both small, about 6% or less. In this respect, the good agreement between experiment and theory, using the self-consistent-field Hartree−Fock cluster approach for heroin, is in keeping with the similar type of agreement found in our recent investigations[8−10] on other physiologically and energetically important molecules. One could therefore utilize the energy levels, electronic wave functions, and electron densities obtained from the Hartree−Fock cluster approach we have used, quite effectively for interpretation of other properties for heroin that may become available in the future, for instance, chemical shifts and indirect spin−spin interactions from nuclear magnetic resonance (NMR) measurements.[18] We therefore present next our predicted results for nuclear quadrupole interaction parameters for ^{17}O and deuteron (^{2}H) nuclei with the hope that they will be determined in the future by NMR or special double-resonance techniques,[19] to enhance signals of small intensity resulting either from low frequencies or low abundance.

Our calculated NQI parameters for ^{17}O and ^{2}H respectively are listed in Tables 3 and 4 using the literature values[20] of $Q(^2H) = 0.00286$ barn and $Q(^{17}O) = -0.02578$ barn. The ^{17}O nuclei are considered to replace the abundant isotope ^{16}O in heroin, whereas the ^{2}H nuclei replace the protons (^{1}H) at the corresponding sites, without any changes in positions of the corresponding atoms and the electron distribution, since no significant changes are expected by replacement of nuclei with different masses but with same nuclear charge. Considering first the ^{17}O nuclei, it can be seen from Table 3, by examining the signs of e^2qQ and magnitudes of both e^2qQ and η, that the results for four of the oxygens can be grouped into two pairs. For O(30) and O(33), the e^2qQ have negative sign and are comparable in magnitude and so are the η, which are both sizable, of the order of 0.5. On the other hand, for O(32) and O(34), the e^2qQ are positive and comparable in magnitude, only about 0.5 MHz smaller than for the ^{17}O nuclei, O(30) and O(33), but the values of η are now substantially smaller, of the order of 0.1. The ^{17}O nucleus in atom O(31) is different from both the pairs O(30,-33) and O(32,34) in that the value of η is now large, essentially close to unity, while e^2qQ has a magnitude close to O(30) and O(33) but of opposite sign. It would be helpful to have experimental results for the nuclear quadrupole interaction parameters for these oxygen nuclei not only to test the quantitative agreement with our results in Table 3 but also to see if they fall into the three distinct categories just discussed. One can however qualitatively understand the groupings of the five oxygens according to their calculated e^2qQ and η, by examining the natures of their bondings with their neighbors and overall environments. Thus O(32) and O(34) are each bonded to a single carbon atom, while O(30) and O(33) are bonded to two carbon atoms, the nature of their environments being also somewhat similar. The atom O(31) is also bonded to two carbons, but these are now part of a five-membered ring instead of a chain as in the case of O(30) and O(33).

Next, from Table 4, one can observe that all the ^{2}H (deuteron) have similar values for e^2qQ and η, the coupling constants (e^2qQ) being small, lying between 0.2 and 0.25 MHz, and the values of η are also rather small, between 0.01 and 0.08. The

TABLE 3: Nuclear Quadrupole Coupling Constants and Asymmetry Parameters for ^{17}O in Heroin

nuclei	e^2qQ (MHz)	η
O(30)	−12.515	0.438
O(31)	12.774	0.971
O(32)	12.050	0.120
O(33)	−12.734	0.583
O(34)	11.861	0.086

TABLE 4: Nuclear Quadrupole Coupling Constants and Asymmetry Parameters for ^{2}H in Heroin

nuclei	e^2qQ (MHz)	η
H(5)	0.227	0.058
H(6)	0.228	0.057
H(7)	0.222	0.061
H(8)	0.223	0.059
H(9)	0.218	0.053
H(10)	0.219	0.044
H(14)	0.219	0.013
H(35)	0.230	0.049
H(36)	0.229	0.036
H(37)	0.229	0.050
H(38)	0.228	0.058
H(39)	0.228	0.044
H(40)	0.226	0.053
H(41)	0.213	0.019
H(42)	0.235	0.063
H(43)	0.213	0.047
H(44)	0.206	0.067
H(45)	0.231	0.066
H(46)	0.233	0.068
H(47)	0.230	0.076
H(48)	0.236	0.087
H(49)	0.226	0.030
H(50)	0.228	0.039

TABLE 5: Effective Charges Associated with Different Atoms in Heroin

nuclei	charge	nuclei	charge
N(1)	−0.284	C(26)	0.585
C(2)	−0.483	C(27)	−0.695
C(3)	−0.346	C(28)	0.674
C(4)	−0.099	C(29)	−0.706
H(5)	0.204	O(30)	−0.481
H(6)	0.196	O(31)	−0.440
H(7)	0.168	O(32)	−0.446
H(8)	0.204	O(33)	−0.502
H(9)	0.185	O(34)	−0.466
H(10)	0.246	H(35)	0.218
C(11)	−0.393	H(36)	0.227
C(12)	−0.139	H(37)	0.218
C(13)	0.081	H(38)	0.227
H(14)	0.277	H(39)	0.216
C(15)	−0.458	H(40)	0.254
C(16)	−0.310	H(41)	0.217
C(17)	0.382	H(42)	0.269
C(18)	0.275	H(43)	0.272
C(19)	−0.158	H(44)	0.248
C(20)	0.085	H(45)	0.229
C(21)	−0.249	H(46)	0.209
C(22)	−0.282	H(47)	0.223
C(23)	−0.646	H(48)	0.227
C(24)	0.345	H(49)	0.202
C(25)	0.022	H(50)	0.199

small values for the e^2qQ for the ^{2}H nuclei are expected because both the quadrupole moment for ^{2}H is small[20] and the valence electron for hydrogen is a 1s electron, with the anisotropy responsible for q and η arising from the distortion of the spherical symmetry around the ^{2}H nucleus from the bonding of hydrogen to its carbon neighbors. The range of calculated values of e^2qQ for ^{2}H is close to the experimental values[21,22] of 0.193 and 0.191 MHz for the e^2qQ of ^{2}H obtained by nuclear magnetic resonance (NMR) measurements in benzene (C_6H_6) and methane (CH_4) molecules, respectively. Also the small asymmetry parameters obtained for all the ^{2}H nuclei in Table 4 suggest that the bonding for all the hydrogen atoms to their nearest carbon atoms are similar to the bonding in benzene or methane where the charge distributions around the ^{2}H are nearly axially symmetric. This near axial symmetry can be understood by looking at the geometry around the hydrogen atoms which are seen to be disposed in a tetrahedral manner (H(5)−H(10), H(35)−H(46), H(49), H(50)) as in methane with respect to the nearest-neighbor carbon atoms or in a trigonal manner (H(47), H(48)) as in a benzene-like ring involving the carbon atoms C(15)−C(18), C(24), and C(25). It would be valuable to have experimental results for the nuclear quadrupole interaction parameters to compare with our results in Table 4 and thus assess the accuracy of the electron distribution in the peripheral regions of the heroin molecule obtained from our Hartree−Fock investigations.

Finally, in Table 5, we have presented the effective charges associated with different atoms, obtained using the Mulliken approximation[23] and the wave function from D95U basis set. It is hoped that these will be useful in understanding the affinities of different molecular groups for various atomic sites and results of future investigations of the X-ray photoemission spectra (ESCA)[24] for the carbon, nitrogen, and oxygen atoms in the heroin molecule.

IV. Conclusion

Our investigations in the present work on heroin show that there is good agreement between theory and experiment[4] for the ^{14}N quadrupole coupling constant and asymmetry parameter in this system. This good agreement has provided encouragement to look for possible sources for resolving the small but significant remaining differences between theory and experiment. One of the possible causes suggested and discussed here is the need for the determination of the positions of hydrogen atoms by neutron diffraction technique[17] or by Patterson synthesis[16] with the help of X-ray diffraction data. This would be helpful to test the accuracy of our calculated electron distributions and its dependence on hydrogen atom positions and also to study the effect on the comparison between theory and experiment for the ^{14}N nuclear quadrupole interaction parameters. The other source suggested is the influence of intermolecular interactions not taken into account in our calculations, which deal with a single heroin molecule. These effects should be studied in the future to analyze their influence on the electric field gradient tensor at the ^{14}N nucleus, although they are expected to be rather time consuming. Also, many-body effects have not been included in our calculation, which is strictly Hartree−Fock in nature. These effects are also expected to be rather time-consuming to investigate, even more so than intermolecular effects. They would however be important to study in the future to see how they influence the good agreement already obtained between theory and experiment for the ^{14}N nuclear quadrupole interaction parameters and to see if they can resolve the small remaining differences. It is also hoped that experimental results will become available in the future on samples with higher purity than the one in which they have been measured[4] to see how they influence the agreement between experiment and theory.

We have also presented the results for the quadrupole coupling constants and assymmetry parameters for the ^{17}O and ^{2}H nuclei with the expectation that experimental data will become available for them by NMR or related methods[19] that would allow comparison with our theoretical predictions. Such a comparison would be very helpful in obtaining a more complete understanding of the electron distribution over the entire heroin molecule than is possible from the nuclear quadrupole interaction of the ^{14}N nucleus alone. Lastly, we have presented the effective charges on the various atoms with the hope that they would be helpful in providing useful insights about the strengths of attachment of different molecular groups in the heroin molecule.

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