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A *First Principles* Investigation of the Structure of a Bacteriochlorophyll Crystal

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Organic crystals offer a unique possibility for experimentally studying molecular structures and intermolecular interactions. As such, they have been rather intensively investigated by the use of *ab initio* based effective potentials[1] or periodic Hartree−Fock calculations.[2] In recent times, the density functional theory (DFT)[3] approach to computation of electronic structure has been gaining popularity in the chemical community for applications to chemically relevant system.[4−8] DFT has been applied recently to the study of organic molecules such as butane,[8] perfluorinated alkanes,[9] or the crystal structure of C_{60}.[10,11]

In this communication we present an *ab initio* study of the crystal of methyl bacteriophorbide (MeBPheo) *a*, a bacteriochlorophyll derivative, and high-precision structure of which is available.[12] Our main purpose has been to investigate the viability of the technique toward complex molecular systems relevant to biologically important phenomena, in this particular case photosynthesis. Here we present the following results: First, we show that DFT is capable of calculating nuclear positions in excellent agreement with the experimental X-ray structure. Second, the calculated electronic density of the HOMO orbital reveals a π type bond between rings I and III, consistent with the one-dimensional chain structure of the MeBPheo *a* molecules in the crystal. Finally, after performing the optimization of the molecular geometry with one electron in the LUMO state, we find localized bond length changes near the ring II of the MeBPheo *a*.

We have performed *ab initio* calculations on one unit cell of the MeBPheo *a* molecular crystal, whose structure belongs to space group *P*1 with one MeBPheo *a* and one benzene molecule in the unit cell which totaled 98 atoms. In line with standard DFT calculations of solids, we expand the single-electron Kohn−Sham orbitals in a basis set of plane waves compatible with the system periodicity. The Brillouin zone of the crystal is sampled at the γ point only. In our scheme only the valence electrons are included explicitly in the calculation. The effects due to atomic core electrons are taken into account by *ab initio* pseudopotentials associated with each atom.[13] In this study, we have used instead supersoft Vanderbilt type pseudopotentials[14] which allow a significant reduction of the energy cutoff and hence of the memory requirements. This choice is essential for the feasibility of our calculation given that the MeBPheo *a* crystal contains 98 atoms.

In the DFT approach, exchange and correlation effects are taken into account by the approximate exchange-correlation functional. Its simplest and most widely used approximation is the local density approximation (LDA). In this study we have included corrections to the LDA which depend on the gradients of the density. Following previous works on water,[6] we employed Becke's gradient correction[15] for exchange only.

In order to obtain the *ab initio* predicted molecular structure of the MeBPheo *a* and of the crystallization benzene contained in the unit cell, we carried out a total energy minimization of the X-ray crystal structure[12] with respect to both electronic and nuclear degrees of freedom, using the Car−Parrinello approach.[16] All calculations were carried out keeping fixed the experimental lattice parameters ($a = 7.184$ Å, $b = 8.073$ Å, $c = 17.071$ Å, $\alpha = 91.04°$, $\beta = 93.50°$, $\gamma = 110.06°$). At this stage the calculation required about 7 days of CPU time on an IBM RISC 590 computer.

If only the heavy atoms contained in the crystal (carbon, nitrogen, and oxygen) are considered, we find an excellent overall agreement between the calculated and X-ray structures. For these atoms the root-mean-square difference between the two structures is about 0.08 Å. Average deviation from experiments are 0.025 Å for bond lengths and 1° for bond angles involving carbons and nitrogens. Bond lengths concerning oxygen atoms differ more, with an average deviation of 0.045 Å. The CO bond lengths were always overestimated, consistent with the initial tests on the CO_2 molecule. We have also compared our structural results against those distinct structural features of the MeBPheo *a* molecule found by X-ray. As shown in Figure 1, we find that the distortion from planarity of the imidazol ring and the alternating pattern of the bond length around the inner ring atoms are well reproduced by our calculation.

The agreement between the calculated and experimental hydrogen positions is poorer. Deviation in bond lengths in particular was sometimes 1 order of magnitude larger than for the heavy atoms. It must be pointed out, however, that protons were determined experimentally from successive difference maps or, in some cases, put in idealized positions. This procedure gave, for instance, for bonds C20−H58, C34−H68, and C44−H89 unlikely C−H lengths smaller than 0.84 Å (see Figure 1a).

To gain insight into the nature of the optically important electronic states, we have calculated the Kohn−Sham eigenvalues and eigenvectors for the occupied levels and for some of the lowest lying unoccupied states. In Figure 2 we show the corresponding electronic density of states near the gap separating occupied and unoccupied orbitals projected along the axis perpendicular to the imidazole ring. This projection weights each state according to its imidazole ring π bond character. From this picture we notice that the highest occupied and the lowest unoccupied molecular orbital (respectively, HOMO and LUMO) are π orbitals. By visualizing the HOMO and LUMO electron densities, we also find that both encompass only atoms which belong to the imidazole ring. Moreover, the probability density of the HOMO, displayed in Figure 3, shows a π type bond between rings I and III of MeBPheo *a* molecules belonging to

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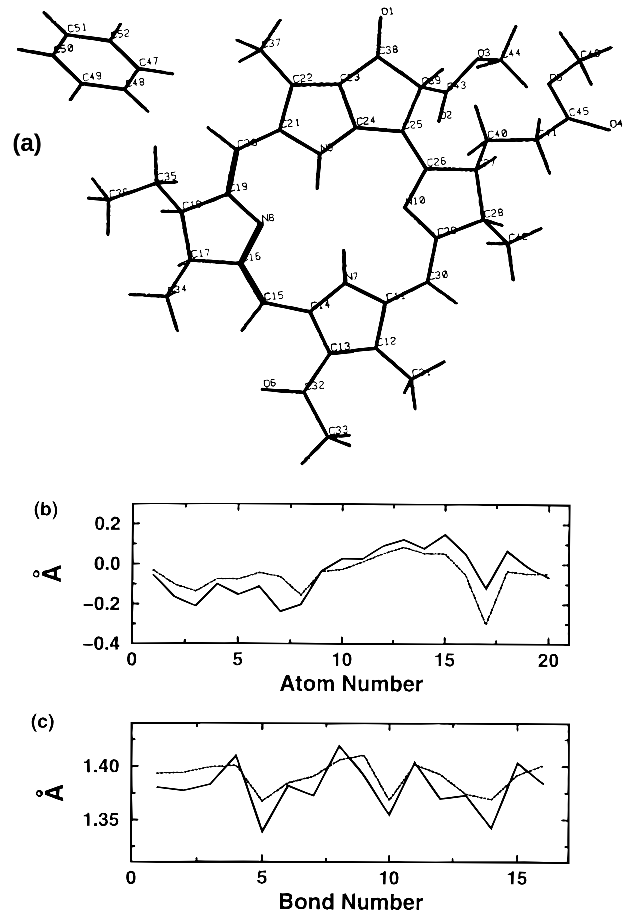

Figure 1. (a) Molecular structure of the MeBPheo *a* and the crystallization benzene molecule. For clarity only heavy atoms (C, O, N) are labeled. The thicker lines show the largest bond length changes obtained from the excited state structural optimization (see text for details). (b) Display of the deviation of the 20 carbon atoms of the macrocycle from the plane defined by the four nitrogens. The continuum and dotted lines represent the X-ray and the *ab initio* results. The plot starts from atom C11 and follows the numbering of the upper figure. (c) Display of the bond distance of the inner ring atoms as obtained from X-ray (continuum line) and calculation (dotted line). The first bond of the plot correspond the covalent bond between atom C11 and N7 of the upper figure.

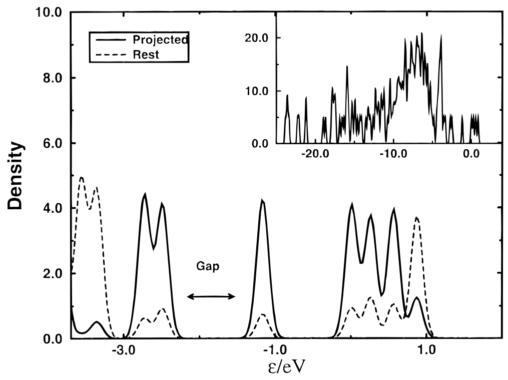

Figure 2. Electronic density of states near the HOMO−LUMO splitting. The solid and dashed lines represent, respectively, the electronic density of the states with ring π character and the residual density. In the inset we show the total electronic density of states.

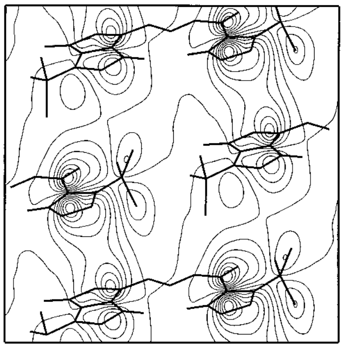

Figure 3. Contour plot of the charge associated with the HOMO on a plane perpendicular to the ring-stacking direction. Only atoms close to the plane were projected into the picture. The contours joining two molecules in the upper right and lower left corners exhibit the formation of an intermolecular bond.

adjacent cells. This intermolecular bond would account for the stacking of MeBPheo *a* molecule to form one-dimensional chains in which ring I and III of successive molecules overlap.

Optical properties of chlorophyll are important for the spectroscopy not only of the isolated chromophores but also of chlorophylls containing proteins. A full investigation of the optical properties of this system is beyond the scope of this work and beyond the realm of applicability of DFT. Notwithstanding, we looked at the possibility that a long lived excited state could induce structural changes. For such an excited state, DFT may offer a reasonable description, and the results can provide useful insight. Thus, we investigated the structural effects of exciting one electron from the HOMO to the LUMO. Starting from the states obtained from the Kohn and Sham matrix diagonalization at the optimized geometry, the electronic state population was restricted to have singly occupied HOMO and LUMO. Then, by relaxation of the electronic and nuclear degrees of freedom, the optimized geometry of this excited state was found. We stress that only states with $S_z = 0$ were dealt with in the calculation. As expected, given the size of the perturbation, only a few bonds were modified by more than 1%. In Figure 1 we plot these bonds with a thicker line. We notice that all the bonds affected by the excited state occur near ring I of MeBPheo *a* molecule. This local structural change could eventually be detected by vibrational spectroscopy of the excited state.

The performance of our DFT approach is remarkably good as compared to more conventional empirical calculations which give a much poorer mean-square deviation from X-ray structure.[17] In the present work we have not optimized the lattice parameters. This is, however, the quantity most easily accessible to experiments, while internal parameters are more difficult to determine. Thus, we can very usefully complement the experimental data. Moreover, the use of the newly developed approach of ref 18 will allow in the near future full relaxation of the structures. In perspective, there is a concrete possibility that with a reasonable effort X-ray crystallography could benefit from our technique and its capability of providing accurate electron densities[19] for crystals of moderate size biological molecules. In future work, issues regarding the correct prediction of excitation energies which are essential for molecular electronic spectroscopy will need to be resolved.

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