Quantum chemical studies of the physics around the metal-insulator transition in (EDO-TTF)2PF6
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CHAPTER 5. COMPARISON OF AB INITIO MOLECULAR PROPERTIES OF EDO-TTF WITH THE PROPERTIES OF THE (EDO-TTF)$_2$PF$_6$ CRYSTAL.$^9$

$^9$The research in this chapter was published in 2010 in Chemical Physics Letters: “Comparison of ab initio molecular properties of EDO-TTF with the properties of the (EDO-TTF)$_2$PF$_6$ crystal”, G.J. Linker, P.H.M. van Loosdrecht, P.Th. van Duijnen, R. Broer, Chem. Phys. Lett., 487 (2010), 220-225

$Ab$ initio quantum chemical calculations were performed for the intrinsic geometrical and electronic structure of EDO-TTF using HF, CASSCF and DFT. Studying one EDO-TTF molecule in vacuum is a first step in understanding its behaviour in the crystal. These in vacuo results are compared with the properties of the (EDO-TTF)$_2$PF$_6$ crystal at near room temperature. It is demonstrated that, by bending and charging the molecule in vacuum, the deformation that is associated with the origin of charge ordering (CO) in this material is an inherent property of the EDO-TTF molecule. Further, it is shown that deformations can be readily made at ambient temperatures.

In the previous chapter, a rationalisation is given for the bent and planar geometry of respectively neutral and positively charged EDO-TTF. In this chapter, conclusive evidence is provided that the intrinsic geometry of the neutral EDO-TTF molecule is bent and that it becomes planar as soon as it becomes positively charged. It is shown that the EDO-TTF molecule is easily deformed.
Chapter 5

5.1 **Computational details**

*Ab initio* HF calculations were performed using the 6-31G** basis set [48] using the MOLCAS package [105]. Spin-restricted HF (RHF) was used for the neutral and +2 charged EDO-TTF molecule and a minimal CASSCF was used for the open shell +1 charged molecule.

For the neutral molecule, sensitivity of the calculated geometrical and electronic properties with respect to basis set and computational method were checked by using the ANO-S basis set and by using CASSCF theory with 12 electrons in an active space of 12 orbitals. The active space was selected by studying HF orbital energies of neutral EDO-TTF using the 6-31G** basis set. Since the HOMO-3 to HOMO-5 are close in energy (within 0.41 eV) and the HOMO-6 is well separated from the HOMO-5 by 1.18 eV it was decided to choose 6 occupied RHF orbitals, *i.e.* up to the HOMO-5 in the active space. This was balanced by also including 6 RHF virtual orbitals into the active space. In the resulting CASSCF wavefunctions, the HF reference has a weight of 75% to 80% depending on the basis set used (ANO-S, 6-31G** respectively). DFT was used to confirm the results of Iwano et al. [132], who studied the electronic structures of the EDO-TTF tetramer. The hybrid B3LYP functional and the 6-31G** basis set was used for these calculations.

Geometry optimisations were performed in MOLCAS using analytical gradients of the energy with respect to nuclear displacements. Partial charges were derived using Mulliken population analysis [11] (MPA) and LoProp analysis [111].

For dimers, we performed ROHF calculations with the 6-31G** basis set. Molecular geometries were taken from the low temperature (insulating phase) X-ray crystal geometries [99].

5.2 **Geometries of neutral EDO-TTF**

In chapter 4, a rationalisation was given for of the inherently bent molecular geometry of neutral EDO-TTF. In this chapter, the PES is explored by performing geometry optimisations at the HF level. The minima are confirmed by performing CASSCF calculations. The minimum on the PES corresponds to a bent geometry, while a local minimum exists that corresponds to a planar geometry (higher in CASSCF energy by 1 cm\(^{-1}\) and 20 cm\(^{-1}\) using respectively the 6-31G** and ANO-S basis set). Using DFT the optimal geometry was found to be bent, but the planar local minimum could not be found. In order to distinguish the two minima, it will be continued to be called a local minimum despite the energy difference being so small that the minima can be considered equal in energy.

Comparing the calculated optimal bent geometries to those observed using X-ray diffraction [99], it is found they are well in agreement, especially noting the considerable anisotropic displacement parameters of the atoms in the EDO moiety in the experimental geometry. The bond lengths, bond angles and dihedral angles of this optimised bent geometry (Table 16 in appendix A) are briefly discussed.

Bond lengths in the CASSCF calculation were generally within 0.04 Å from experiment, with the exception of the C-S bond lengths from the central carbon atom in the C\(_3\)S\(_2\) ring (+0.06 Å), and the single carbon bond in the ethylene group (+0.05 Å). The geometry also exhibits a small skewing in the EDO moiety where the two oxygen bound carbon to sulphur bonds are unequal in length (+0.01 Å and +0.04 Å). This was not resolved in the experimentally obtained structure. This effect in the CASSCF geometry is also absent in our HF geometries where bond lengths are within 0.03 Å of the experiment, again with exception of the single carbon bond in the ethylene group (+0.05 Å).
single carbon bond was even longer (+0.06 Å) in our DFT geometry where all other bond lengths were within 0.04 Å from experiment. All bond angles in the calculated geometries are within 3° from experiment. The dihedral angles in the geometries obtained in our CASSCF and HF calculations are very well in agreement (within 2°) with experiment. A notable exception is the (ethylene)-OC dihedral angle that is found to be 4° larger in these calculations. The angles obtained from our DFT calculations are within 6° from the experiment and show a more bent geometry.

HF calculations were also performed with smaller basis sets (STO-3G, 3-21G, 4-31G, 6-31G and 6-31G*). From these calculations, the bent geometries are not reproduced. It is important that sufficiently large basis sets like ANO-S are used in order to reproduce the bent geometry of the EDO-TTF molecule.

5.3 Positively charged EDO-TTF

The changes to the molecular orbitals in the ionised EDO-TTF molecules were studied in ∆SCF calculations using the 6-31G** basis set. Using the planar local minimum geometry of the neutral molecule, electrons were extracted from the molecule without allowing the geometry to relax. In ionising EDO-TTF, the characters of the highest filled molecular orbitals stay the same (Figure 34). The first ionisation energy is 6.2 eV. The electron is extracted from the HOMO, a π-type orbital that has predominant contributions from the out-of-plane $p_z$ functions on the central two carbon atoms and from those on the sulphur atoms. The second ionisation energy is 11.1 eV. Note that the π orbital becomes the LUMO in the +2 charged molecule, in which the lowest state is a closed shell singlet. A triplet and an open shell singlet state exist at a higher energy, with the HOMO and HOMO-1 each occupied with one electron. From a state-average 2 electrons in 2 orbitals CASSCF calculation, using the 6-31G** basis set, it was estimated that the separation of the closed shell and open shell singlet is 5.3 eV. The closed shell singlet was continued to be studied since it is lowest in energy in the +2 charged molecule.

If the geometry is allowed to relax, the electron removal energies become 5.8 eV and 10.3 eV respectively. Exploring the PES for the +1 and +2 charged EDO-TTF molecule always a planar geometry was found. Using DFT, using the same basis set, the planar optimal geometries were confirmed.
As can be seen from Figure 34, the doubly occupied HOMO in +2 charged EDO-TTF has no charge density at the central double carbon bond and as it is demonstrated in the next section the terminal C₃S₂ ring becomes free to rotate. The optimal geometry is one where a significant rotation of 37° exists over this central carbon bond.

Confirming the observation by Aoyagi et al. [109] that the holes are localised on sulphur atoms, our charge analysis showed that charge density is indeed predominantly removed from the central region of the molecule. Population analysis with the MPA and the LoProp method demonstrated that, on extracting an electron from the neutral EDO-TTF molecule, a charge of +0.7 is formed on the four sulphur atoms collectively. Extracting another electron from the molecule increases this charge on the sulphurs by 0.7 to +1.4.

5.4 Charge ordering in (EDO-TTF)₂⁺ dimers
From ab initio cluster calculations on (EDO-TTF)₂⁺ dimers it follows that the hole only delocalises over planar molecules, and that bent molecules tend to stay neutral. This constitutes a confirmation of the strong molecular geometry to charge relation: neutral molecules are bent, positively charged molecules are planar.

Table 2: ROHF HOMO and charge ordering for three (EDO-TTF)₂⁺ dimers. P and B denote planar and bent molecules respectively.

<table>
<thead>
<tr>
<th>HOMO</th>
<th>Charge Ordering</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>+0.50</td>
</tr>
<tr>
<td>BP</td>
<td>+0.05</td>
</tr>
<tr>
<td>BB</td>
<td>+0.95</td>
</tr>
</tbody>
</table>

In Table 2, the location of the hole in different (EDO-TTF)₂⁺ clusters is shown. The molecular charge ordering (CO) is derived from the character of the highest occupied dimer orbital (we will henceforth use the molecular term HOMO instead) from which one electron was extracted, and also from Mulliken charge analysis. Three geometrically different positively charged dimers are considered: PP, BP and BB. The letters of the dimer name indicate the geometry of the molecules: P for planar and B for bent. Only in the PP dimer the positive charge is delocalised over both molecules. In the BB dimer, that contains two bent molecules, the hole localises on one molecule with a CO of (0.95, 0.05) in which each number represents a molecular charge. The same CO is obtained for the BP dimer, in which the hole localises nearly fully on the planar molecule. It shows that bent molecules tend to remain neutral, and that planar molecules adopt the positive charge.

5.5 Deformations
The change in total energy of deformations was studied by keeping all bond lengths fixed, and by applying a rotation of the C₃S₂ ring over the central double carbon bond, or by applying a bending of the EDO-TTF molecule. The results demonstrate that, classically speaking, both deformations can be made at considerable angles with energies available at the temperatures at which the experimental geometries were obtained. All calculations were done using the 6-31G** basis set, and with HF theory.

5.5.1 Rotation of the C₃S₂ ring over the central C=C bond
A path on the PES for EDO-TTF molecules with charge 0 and +1 was investigated, using RHF and ROHF theory respectively and the 6-31G** basis set, by starting with the planar geometry (Φ=0°) at the local minimum on the PES. A rotation was allowed of the terminal C₃S₂ ring over the central C=C
double bond (Figure 35). When applying a higher positive charge to the molecule, the rotation becomes easier. With higher positive charge, the C=C bond becomes longer and, as can be seen in Figure 34, at charge 2, the HOMO has no charge density in this region. In the metallic phase, at the temperature at which the experimental geometry was determined (300 K), there is enough thermal energy to classically allow rotations of approximately 8° and 13° for the molecules of charge 0 and +1 respectively.

![Figure 35: Rotation of the terminal C₃S₂ group for molecules with charge 0, +1 (a) and +2 (b). ΔE is the relative total energy.](image)

The optimal geometry of the +2 charged molecule is rotated 37° over the central C=C bond (Figure 35b). To rotate the terminal C₃S₂ group back to a planar molecule, 368 cm⁻¹ is needed. At an angle of -2°, there is a maximum of 372 cm⁻¹. A local minimum of 131 cm⁻¹ at -35° is also found.

![Figure 36: Rotation over the central C=C double bond in C₂H₄, C₂S₄ and EDO-TTF for the neutral (a), +1 charged (b) and +2 charged (c) molecules. For all molecules and charges the energy offset is set at Φ=0°.](image)

These rotation angles were compared to calculations on the model systems ethylene and C₂S₄ (Figure 36), using the same basis set and level of theory. The following observations were made. In the neutral EDO-TTF molecule (Figure 36a), the central C=C bond is less stiff than that in ethylene or C₂S₄. For example, at an angle of 8° the rotation energies for EDO-TTF, C₂S₄ and C₂H₄ are respectively 223, 286 and 324 cm⁻¹.

When one π electron is removed from the EDO-TTF molecule, part the electron is extracted from the central C=C bond. The bond does not become as weak as in C₂H₄⁺ (Figure 36b) because the π-MO has also amplitude on the sulphur atoms and hence part of the electron density is removed from
the four sulphur atoms. In comparison, the stiffness of the C=C bond increases slightly in C$_2$S$_4^+$ compared to the neutral C$_2$S$_4$ molecule. On extracting two electrons from the molecules, EDO-TTF$^{2+}$ becomes yet easier to rotate however not as much as in ethylene$^{2+}$ where the bond is now single and where there is a significant energy gain when making an angle up to 90° Figure 36c).

5.5.2 Bendings out of the molecular plane
The reported experimental geometries of neutral EDO-TTF by Ota et al. [99] can be seen as bent at two angles $\Phi_1$ and $\Phi_2$ (inset Table 3) at various degrees. Applying these bendings to our planar HF structures at the local minimum, the total HF energy was calculated for molecules at different positive charge using the 6-31G** basis set. The results are shown in Table 3. Some care should be taken interpreting some of the small energy values in Table 3 as they are comparable to the zero point vibrational energy that was computed in neutral EDO-TTF as 30 cm$^{-1}$.

Table 3: Rise in total HF energy when applying experimentally observed [99, 124] bending angles to our optimised geometries for molecules of different positive charge.

<table>
<thead>
<tr>
<th>$\Phi_1$, $\Phi_2$</th>
<th>geometry</th>
<th>charge</th>
<th>charge</th>
<th>charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6.0, 0.3)</td>
<td>(M-phase)</td>
<td>0</td>
<td>106</td>
<td>216</td>
</tr>
<tr>
<td>(11.1, 7.9)</td>
<td>B (I-phase)</td>
<td>+1</td>
<td>545</td>
<td>1114</td>
</tr>
<tr>
<td>(0.8, 2.1)</td>
<td>P (I-phase)</td>
<td>+2</td>
<td>14</td>
<td>30</td>
</tr>
</tbody>
</table>

There is a slight rise in total HF energy when applying the angles. The total HF energy was increased by only 4 or 106 cm$^{-1}$ for the molecule at the geometry as observed in the metal (M) phase when a charge of 0 or +1 was applied respectively. The B and P geometries observed in the insulating (I) phase are associated with a neutral and a +1 charged molecule respectively and applying the bending reported for these geometries lead to a rise of 18 and 14 cm$^{-1}$ in total HF energy. Note that it takes far more energy (545 cm$^{-1}$) to adopt a geometry with angles in the B geometry at charge +1, than applying the bending angles found in the P geometry (13 cm$^{-1}$). The energies required to make these bent deformations are small compared to the energy available at the temperatures at which the measurements took place (kT ≈ 200 cm$^{-1}$ at 300 K).

To study the effect of bending the molecule more systematically, another path on the PES was studied by bending the molecule for different positive charges (Figure 37), keeping $\Phi_1 = \Phi_2$. It takes more energy to bend molecules with increasing positive charge. The C-S bond lengths decrease when electrons are extracted indicating a higher bond order and tighter bonds. Classically speaking, at ambient temperatures, bent geometries can be made of 4°, 6° and 18° for respectively a +2, +1 and a 0 charged molecule. Therefore, when energy around room temperature is available, the molecule can be easily bent. The lower the positive charge of the molecule, the easier it is for the molecule to adopt a bent geometry. A bent geometry is observed in the insulating phase, and it is associated with a neutral molecule. Our optimised bent geometry shows that this deformation is indeed intrinsically stabilised.
5.6 Discussion

The geometrical and electronic structure of an isolated EDO-TTF molecule was studied by a series of HF, CASSCF and DFT calculations. The results are of relevance for crystalline EDO-TTF$_2$PF$_6$ and, more indirectly, also for various other TTF derivatives. From the *ab initio* calculations, it was concluded that EDO-TTF is an inherently bent molecule. The HOMO in the neutral isolated EDO-TTF molecule is responsible for the bent geometry. Removing electrons from this MO, *e.g.* by ionisation or excitation, leads to a planar geometry. This planar geometry also corresponds to a local minimum on the PES for the neutral molecule in its ground state. Comparing the calculated optimal bent geometry with the experimental X-ray diffraction geometry of the crystal, it was found that they are in very good agreement. Calculations on the (EDO-TTF)$_2^+$ dimers confirm the charge to molecular geometry relation. Neutral molecules in the dimers tend to adopt the hole. The positive charge delocalises over a dimer with two planar molecules, whereas in a dimer that consists of two bent molecules, the positive charge localises one of the two molecules.

The observation by Aoyagi *et al.* [109] is confirmed that the π electron that is donated by EDO-TTF to PF$_6$ is predominantly extracted from the central tetrathia region. It is demonstrated that after ionisation 70% of the hole is localised on the sulphur atoms while the remainder is delocalised over the molecule.

Very little energy is needed to deform the molecule. At ambient temperatures, enough energy is available to rotate at significant angles over the central carbon double bond, or to bend the molecule. The energies required to make deformations are actually so small that it leads us to the conclusion that discussing CO only in terms of these geometrical deformations is not fruitful. Our results confirm the assignment of +1 charge to a planar geometry and a zero charge to a bent geometry, as is commonly done in the literature. However it is surprising that the bent inherent geometry of neutral EDO-TTF in vacuum at 0 K remains in the electron donor layers of the crystal at room temperature. The crystal field and other environment effects seem to not change the inherent geometry of the molecule.

In a recent DFT study [132] on the EDO-TTF tetramer, it was suggested that the mechanism behind the CO is electrostatic in nature. That electrostatic interactions between cation and anion play an important role in the M-I transition was also suggested by Sakata *et al.* [120] from uniaxial strain experiments. In these experiments, the M-I transition was assisted when strain was applied along the inter-donor layer direction. It is likely that the primary effect is the redistribution of electrons and that the electrostatic consequences stabilise the geometry to give rise to a particular geometry and CO at low temperature. In this insulating low temperature phase, an excitation exists that leads to metallic behaviour. At higher temperature, the photo-excitation disappears suggesting that at that temperature the ground state is metallic and the EDO-TTF monomers become planar.
PART III: CONDENSED PHASE

In this part of this thesis, several properties of the condensed phase of (EDO-TTF)$_2$PF$_6$ are discussed. The knowledge of molecular properties, as researched in Part II, can be used when considering properties of molecular crystal. In general, some of the properties of molecular crystals find their origin in the molecules and others will be shown to be a consequence of the unit cell, the smallest repeating unit in a crystal. Yet other properties are due to the condensed phase as a whole.

I will show that one molecular property is of crucial importance for the physics of (EDO-TTF)$_2$PF$_6$. It is the direct relationship between the molecular shape and the molecular charge. The co-existence of neutral, planar molecules and charged, bent molecules in the crystal is at the heart of the physics of the M-I transition in this material. It is shown from electronic band structure calculations in chapter 7 that the conduction anisotropy of the high temperature phase of (EDO-TTF)$_2$PF$_6$ is quasi-one-dimensional (Q1D), and that the electronic structure is unstable with respect to a symmetry lowering deformation: a Peierls instability. The symmetry lowering of the electronic structure, and also of the geometry, allows two types of molecules to co-exist in the unit cell. The charged and neutral molecules adopt their inherent molecular planar and bent geometries.

In forming a tetramer unit cell at lower temperatures, the positive charges that are delocalised in the high temperature phase, localise to form a charge ordering. There are several ways in which two holes can distribute over the four EDO-TTF molecules of a tetramer unit cell and form the ground state. In chapter 6, the 0110 charge ordering is found for the low temperature structure by using a closed shell wavefunction. For the high temperature structure, a $\frac{1}{2}\frac{1}{2}\frac{1}{2}\frac{1}{2}$ charge distribution is found. It is shown that states with other charge ordering patterns are close in energy.

A further exploration of instabilities involved in the M-I transition is the subject of chapter 8. The effect of the two main deformations of the high temperature structure is studied: anion and cation dimerisation. I show that a dimerising (EDO-TTF)$_2$ stretching displacement leads to the charge ordered state. Also in chapter 8, the possibility for another ground state is explored by studying triplet instability.

Supplement A and B contain a detailed study of the electronic band structures of two other examples of the material class: TTF-TCNQ and the Bechgaard salt (TMTSF)$_2$PF$_6$. These studies provide a background to the studies of the electronic structure of (EDO-TTF)$_2$PF$_6$. Although these materials might look similar to (EDO-TTF)$_2$PF$_6$, they show a different physics.