Quantum chemical studies of the physics around the metal-insulator transition in (EDOTTF)2PF6
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In this chapter, the planar and off-planar geometrical conformations of the EDO-TTF molecules are explained by using our extension of the Debye polarisability model for the bond angle. It is rationalised why EDO-TTF molecules become planar when charged. In fact, it is demonstrated that, in general, this model gives a direct relationship between the electronic polarisability of the atoms and the bond angle.

![Schematic representation of the relation of polarisability of the chalcogen atoms to the molecular geometry of EDO-TCF.](image)

**Figure 23:** Schematic representation of the relation of the polarisability of the chalcogen atoms to the molecular geometry of EDO-TCF.

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8 The research in this chapter was published in 2012 in Physical Chemistry A: "Off-Planar Geometry and Structural Instability of EDO-TTF Explained by Using the Extended Debye Polarizability Model for Bond Angles", G.J. Linker, P.Th. van Duijnen, P.H.M. van Loosdrecht, R. Broer, Phys. Chem. A 116 (2012), 7219-7227
4.1 Introduction

The geometrical structure of EDO-TTF is dictated by its four sulphur bond angles and these are, in turn, determined by the polarisability of the sulphur atoms, as indicated in Figure 23. With HF and MP2 calculations on EDO-TTF, TTF, H₂S and their oxygen and selenium substituted counterparts, our explanation is confirmed. The extended Debye polarisability model for bond angles relates directly the optimum bond angle with the polarisability of the centre atom. No quantum mechanics, nor \textit{a priori} assumptions of hybridisation, nor arguments about orbital repulsion are needed in the Debye polarisability model [3]. Instead, the observable polarisability of the electron distribution is recognised and, as it will be shown, induction effects due to it are stabilising. Considering (EDO-TTF)_2PF_6 in this light proves to be very fruitful.

There are alternative models for the bond angle in which \textit{e.g.} quantum mechanics or hybridisation are used. In itself that is not a reason to develop a new model. Our extended Debye polarisability model for the bond angle is attractive because it can predict trends in bond angles when relative changes in ‘atomic’ polarisability are considered. In this chapter, we prove it is ideally suited to explain the differences in molecular geometry of neutral EDO-TTF and the EDO-TTF⁺-ion. Alternative models for the bond angle include the widely taught Valence Shell Electron Pair Repulsion (VSEPR) model [91]. Taking the bond angle in H₂O as an example, repulsion arguments are used in this model to explain the angle. All bonds and lone pairs of valence electrons are considered to be mutually repulsive. The angle for H₂O forms by \textit{a priori} assuming sp³ hybridisation, so the electron pairs arrange in a tetrahedron with angles of 109.2°. To arrive at the water angle of 104° the lone pairs are thought to repel more than the electrons in the O-H bonds, allowing the \( \theta_{H-O-H} \) angle to become sharper. It is a common assumption that the lone pairs are directed outward from oxygen, but actually the H₂O electron density is not far from spherical (figure 24). The only distortions are due to the hydrogen atoms that can be seen as drawn into the electron density of oxygen. The small anisotropy of the polarisability is a good indication for the nearly spherical electron density. From accurate CCSD calculations [106], and with the definition for the anisotropy \( \zeta = (\alpha_{\text{max}} - \alpha_{\text{min}})/\bar{\alpha} \), where \( \alpha_{\text{max}}, \alpha_{\text{min}} \) are respectively the largest and smallest eigenvalues of the polarisability tensor, and \( \bar{\alpha} \) the average polarisability, the anisotropy was calculated as 0.094. It is hard to consider the repulsion of the lone pairs when they do not seem to be directed.

![Figure 24: Isosurfaces of the Hartree-Fock electron density of H₂O (from left to right \( \rho = 0.04, 0.1, 0.2 \)).](image)

The organisation of this chapter is as follows. After a section with computational information, the Debye polarisability model is presented and our extension of it. The model is tested using a series of small molecules in section 4.6. Using our model, the off-planar geometry of TTF is rationalised. Next, the geometry of EDO-TTF is discussed by considering the addition of an EDO group to one side of the TTF molecule. The change in geometry is discussed in terms of chemical doping. Before the conclusion and discussion are presented, two sections will deal with the transition angle at which the neutral and ionised TTF molecules become off-planar. All geometrical features are discussed in the context of the extended Debye polarisability model and are found to be well explained by it.
4.2 Computational information

*Ab initio* calculations are performed to study the effect of induction on the geometry. These calculations are performed at the HF level of theory (spin-restricted open shell HF for ionised molecules) using the ANO-S basis set [73]. All calculations were performed with the MOLCAS [105] package.

Induction effects relate to perturbing the electron density in response to an electric field, therefore the wavefunction needs to be sufficiently flexible. Firstly, the basis set needs to be sufficiently large to allow flexibility to the wavefunction to describe perturbations. Polarisability is underestimated when smaller basis sets are used and that leads to reduced induction effects. Secondly, the level at which electron-electron interactions are modelled is an important factor. In HF theory, the mean field approximation is used. By using MP2 theory part of the dynamical electron correlation is recovered and this improves the simulation of induction effects considerably. Because we need to model the induction effects and not explicitly calculate the polarisabilities themselves, the HF level of theory and the ANO-S basis set was chosen for the calculations on TTF and EDO-TTF. With this choice, the aim is to balance accuracy and computational effort. For a detailed study of the geometry of EDO-TTF at the CASSCF and DFT level I refer to chapter 5. The calculations on small molecules are performed at the MP2 level using the RHF/ROHF wavefunction as reference. The molecules H$_2$Te, H$_2$Po, SbH$_3$, BiH$_3$ are modelled using the relativistic ANO-RCC basis set. Scalar relativistic effects are taken into account by using the Douglass-Kroll-Hess transformation of the Hamiltonian [25, 55].

The atomic polarisabilities used in the Debye model (Table 1) are taken from the library of the discrete reaction field program: DRF90 [125]. Some of these are optimised to reproduce molecular polarisabilities of a series of molecules [79], others are taken from atomic calculations.

Our extension of the Debye polarisability model was implemented in Mathematica and we used this implementation in the analysis of optimum angles.

<table>
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<th>$\alpha$ (bohr$^3$)</th>
<th>Atom</th>
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<td>Bi</td>
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<td>P</td>
<td>29.83</td>
<td>Sb</td>
<td>54.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Atomic polarisabilities $\alpha$ (bohr$^3$) taken from the DRF90 library.

4.3 The Debye polarisability model

In 1929, Debye used a simple electrostatic model [3] to make the dipole moment of H$_2$O and its bent structure plausible. For the general A$_2$B systems the same model is used and extended.

In the Debye model, the polarisability of electron density is recognised. When molecular polarisability is split, arbitrarily, into atomic parts, a molecule can be viewed as a set of polarisable atoms or ions. These respond to the electric field due to the rest of the molecule. The induced electric moments thus formed have interaction with the field. Debye recognised that in H$_2$O the induction energy increases with smaller bond angle, and that it is counteracted by Coulomb repulsion between the two partially charged protons. The present interest is the stability of the general A$_2$B molecule with respect to changes in the bond angle and to the ratio of the polarisabilities of A and B.
In the model for A2B, for A\(^+\)q and B\(^-\)2q hard spheres of radius \(R_A\) and \(R_B\) are taken respectively, fixing the bond length to \(R= R_A + R_B\). The classical relation between radius and polarisability of a conducting sphere is used (appendix F). This means that the atomic polarisabilities are \(\alpha_A = R_A^3\) and \(\alpha_B = R_B^3\).

With this, polarisability is associated with volume and hence with the bond length \(R\). In contrast, in polarised-ion models this connection is not realised. The used parameters \(\alpha\) and \(R\) are independent model parameters. Furthermore, the polarisabilities used in these models are for ionised atoms. They are much smaller than those of neutral atoms. Actually for a qualitative model like ours it is sufficient to recognise that atoms are polarisable and it is only the ratio of the polarisabilities that is important. The calculated relative energy depends on the geometry, in which only the bond angle \(2\theta\) (Figure 25) is varied. Independent variations of the bond length are not allowed in the model.

Assuming linear response and approximating the polarisability of atom \(i\) as a point polarisability \(\alpha_i\), a point dipole moment \(\vec{\mu}_i = \alpha_i \vec{F}_i\) is induced at the expense of polarisation energy \(U_{pol}^i = + \frac{1}{2} \alpha_i F_i^2\).

Three types of interactions are allowed between the atoms in the model. Using \(i\) and \(j\) as atom labels, the interaction energies are \(U_{qq}^{ij}\) for charge-charge interactions, \(U_{qd}^i\) for the interaction of the induced dipole \(i\) with its inducing field and \(U_{dd}^{ij}\) for the dipole-dipole interaction:

\[
U_{qq}^{ij} = \frac{q_iq_j}{R_{ij}}
\]

\[
U_{qd}^i = -\vec{\mu}_i \cdot \vec{F}_i = -\alpha_i F_i^2
\]

\[
U_{dd}^{ij} = -\frac{1}{R_{ij}^3} \left( \vec{\mu}_i^\dagger \vec{R}_{ij} \vec{R}_{ij}^\dagger \vec{\mu}_j - \frac{3}{R_{ij}^2} \vec{\mu}_i^\dagger \vec{1} \vec{\mu}_j \right)
\]

Note that in the expression for \(U_{dd}\), \(\vec{1}\) represents the unit matrix.

With the polarisation energy and the interaction energies the models can be built. First, the original Debye model is presented where a dipole is induced only on the central atom. Next, the model is extended to allow induction on all three centres and in which we allow all interactions.

### 4.4 The original Debye polarisability model

By only considering induction on oxygen in H\(_2\)O, Debye made its bent structure plausible. By setting \(\alpha_A = 0\), the original Debye polarisability model is obtained. \(R\) becomes equal to \(R_B\), thereby reducing atoms A to point charges. The electric field at B is \(F_{B,x} = 0\); \(F_{B,y} = \frac{2q \cos \theta}{R^2}\). Using Eqs. 59a and Eqs. 60-62, the total energy \(U_{Debye}\) becomes:
\[ U_{\text{Debye}} = U_{qq}^{BA1} + U_{qq}^{BA2} + U_{qq}^{A1A2} + U_{\text{pol}}^{B} + U_{qd}^{B} \]
\[ = \frac{q^{2}}{R} \left( \frac{1}{2\sin\theta} - 4 - \frac{2\alpha_{B}\cos^{2}\theta}{R^{3}} \right) \]

To find the extremes, the total energy is differentiated with respect to \( \theta \):

\[ \frac{\partial U_{\text{Debye}}}{\partial \theta} = \frac{q^{2}}{R} \left[ -\cos\theta - 4\alpha_{B}\cos\theta\sin\theta \right] = -\frac{q^{2}}{R} \cos\theta \left[ \frac{1}{2\sin^{2}\theta} - \frac{4\alpha_{B}\sin\theta}{R^{3}} \right] \]

Requiring \( \frac{\partial U_{\text{Debye}}}{\partial \theta} = 0 \) gives for the minimum:

\[ \left[ \frac{1}{2\sin^{2}\theta} - \frac{4\alpha_{B}\sin\theta}{R^{3}} \right] = 0 \rightarrow \sin^{3}\theta = \frac{1}{8}\frac{\alpha_{B}}{R^{3}} = \frac{1}{8} \]

A plot of the energy vs. the angle in Figure 26 shows clearly, the repulsion of the \( A^{aq} \) ions dominate at small angles. At large angles, the induction energy is small because the resulting field at B vanishes and in \( U_{qq} \) the repulsion is dominant. The linear structure corresponds to a maximum. From Eq. 65 it follows that the minimum in the original Debye model is at \( \Theta = 30^\circ \) which corresponds to a bond angle \( 2\Theta = 60^\circ \).

4.5 The extended Debye polarisability model

Extending the Debye polarisability model to include induction on all atoms of \( A_{2}B \), the finite size of the A atoms needs to be recognised: \( \alpha_{A} > 0 \) and \( R = \frac{3}{\sqrt[3]{\alpha_{A}}} + \frac{3}{\sqrt[3]{\alpha_{B}}} \). For convenience only, we take \( \alpha_{B} = 1 \) and \( \alpha_{A} = \beta \). The first consequence of the finite size of the A atoms is that there is a minimum angle: \( \sin \theta_{\text{min}} = \frac{3\beta}{1 + \sqrt[3]{\beta}} \) (Figure 28), where the minimum bond angle (dashed line) \( 2\theta_{\text{min}} \) is plotted against \( \beta \). Besides the electric field on atom B, also the field on atoms A1 and A2 now play a role. For Eqs. 59a-c we write:

\[ F_{A1} = \frac{q}{R^{2}} \left( 2\sin\theta - \frac{1}{4\sin^{2}\theta} \right) \]
\[ F_{A2} = \left( -\frac{F_{A1x}}{F_{A1y}} \right) \]
\[ F_{B} = \frac{q}{R^{2}} \left( 0 \right) \]

With these electric fields (Eqs. 66-68), the total energy \( U_{\text{Debye}+} \) can be calculated as

\[ U_{\text{Debye}+} = U_{qq} + U_{\text{pol}} + U_{qd} + U_{dd} \]
in which all energy terms have contributions from all three atoms. Recognising that the induction energy at atom \( i \) is \( U_{\text{ind}}^i = U_{\text{pol}}^i + U_{qd}^i = -\frac{1}{2} \alpha_i \rho_i^2 \) we get:

\[
U_{\text{Debye}+} = U_{qq} + U_{\text{ind}} + U_{dd}
\]

with

\[
U_{qq} = \frac{q^2}{R} \left( -4 + \frac{1}{2 \sin \Theta} \right)
\]

\[
U_{\text{ind}} = -\frac{2 q^2}{R^4} \left( \cos^2 \Theta + 2 \beta - \frac{\beta}{2 \sin \Theta} + \frac{\beta}{32 \sin^4 \Theta} \right)
\]

\[
U_{dd} = \frac{q^2 \beta^2}{R^7} \left( \frac{-16 \cos^2 \Theta}{\beta} + \frac{3 \cos \Theta}{\beta \tan \Theta} + \frac{1}{2 \sin \Theta} + \frac{1}{2 \sin^3 \Theta} - \frac{1}{4 \sin^4 \Theta} + \frac{1}{64 \sin^7 \Theta} \right)
\]

Using Eqs. 71-73 in Eq. 70, and expressing the total energy in terms of \( \beta \) and \( \Theta \) we get

\[
\frac{U_{\text{Debye}+}}{q^2} = \frac{1}{(1 + 3 \sqrt{\beta})} \left( -4 + \frac{1}{2 \sin \Theta} \right) - \frac{2}{(1 + 3 \sqrt{\beta})^4} \left( \cos^2 \Theta + 2 \beta - \frac{\beta}{2 \sin \Theta} + \frac{\beta}{32 \sin^4 \Theta} \right) + \frac{(-16 \cos^2 \Theta)}{\beta} + \frac{3 \cos \Theta}{\beta \tan \Theta} + \frac{1}{2 \sin \Theta} + \frac{1}{2 \sin^3 \Theta} - \frac{1}{4 \sin^4 \Theta} + \frac{1}{64 \sin^7 \Theta}
\]

Since this is a qualitative model, the partial charges \( q \) of the atoms are viewed merely as the sources for the electric field. it is not the strength of the field but its presence and structure are important. We analyse further using \( q = 1 \). In Figure 27, the individual contributions and the total energy are plotted as a function of the angle \( \Theta \) by using our Mathematica implementation of our model.

Around the optimum angle, all interaction terms are stabilising when \( \beta = 1 \). Going to smaller angles the total energy rises sharply, mainly due to the dipole-dipole repulsion. It is noted that at angles smaller than \( \Theta_{\text{min}} \) no analysis should be performed.

**Figure 27: Total energy (left;) and its components (right; \( \beta = 1 \)) as function of \( \Theta \).**

The minimum of the total energy depends on \( \beta = \frac{\alpha_a}{\alpha_B} \) (Figure 28). At values of \( \beta \) larger than approximately 2.5, the optimum bond angle is 180°. With smaller values of \( \beta \), the optimum angle decreases. The following conclusions are drawn. The bond angle decreases with larger polarisability \( \alpha_B \). With larger polarisability \( \alpha_A \) the bond angle increases.
Figure 28: Optimum bond angle \( (2\theta) \) as a function of \( \beta = \alpha_A/\alpha_B \). Dashed line is the minimum bond angle \( \theta_{\text{min}} \). The two curves represent the extended Debye polarisability model and DRF results.

The model can be improved by using the DRF [125] method, in which the many-body polarisation is treated self-consistently. Induced moments generate fields that in turn induce moments at other polarisabilities, and so on \textit{ad infinitum}. Hence, depending on the molecular geometry, effective polarisabilities [125, 130] appear which in general differ from the nominal values as used in the extended Debye model. The optimal angles derived with the extended Debye polarisability model therefore differ slightly from those derived using the DRF method (the Debye+ and DRF curves in Figure 28).

After showing theoretically that the Debye polarisability model can be used to qualitatively predict bond angles, its validity is tested by considering the bond angle in a series of small molecules.

4.6 Bond angles in small molecules

The dependency of the bond angle on the polarisability is validated using the following series of molecules: \( \text{H}_2\text{X} \in \{\text{O}, \text{S}, \text{Se}, \text{Te}, \text{Po}\} \), \( \text{XH}_3 \in \{\text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}\} \), \( \text{XO}_2 \in \{\text{N}, \text{S}, \text{Se}\} \), \( \text{AsX}_3 \in \{\text{F}, \text{Cl}, \text{Br}\} \). In all series, the polarisability of \( \text{X} \) increases.

The MP2 bond angles (Figure 29) are all within 1.4° of the experimental angles [113]. Angles obtained at the HF level were up to 2 degrees larger than those obtained with MP2. The exceptions are \( \text{SO}_2 \), \( \text{SeO}_2 \) and \( \text{AsF}_3 \) which are up to 1 degree smaller and \( \text{NO}_2 \) which is 4 degrees larger. The experimental values for \( \text{H}_2\text{Po}, \text{SbH}_3 \) and \( \text{BiH}_3 \) were not available.

The conclusion from the original Debye polarisability model, that bond angle decreases with increasing polarisability of the central atom, is clearly confirmed in the \( \text{H}_2\text{X} \) and \( \text{XH}_3 \) series. The prediction of the geometry of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) is surprisingly accurate. The geometry of \( \text{NH}_3 \) is also well predicted and the trend to smaller angles with higher polarisability is observed in the \( \text{XH}_3 \) series. Note that a larger deviation from 120° corresponds to a more pyramidal geometry. The \( \text{AsX}_3 \) series confirms the additional conclusion drawn from the extended Debye polarisability model: with more polarisable outer atoms the bond angle is larger. These trends, without exceptions, were also found at the HF level in a set of over 140 \( \text{A}_2\text{B} \) molecules (appendix C).

The series presented in Figure 29, contain molecules with one or two lone pairs on the central atom. All these molecules are non-linear or pyramidal. When all valence electrons of the central atom are engaged in bonding, the geometry becomes linear or planar. \( \text{CO}_2 \) is an example of such a linear...
molecule. Group-13 tri-halides, AlCl$_3$, AlF$_3$, BF$_3$, are examples of planar molecules, as are SO$_3$ and SeO$_3$. In molecules without non-bonding valence electrons on the central atom, and where the atom has many inner shell electrons, these inner electron shells may be sufficiently polarisable to enable a bent geometry. The group-2 hydride BaH$_2$ is an example of such a molecule [101].

When all valence electrons participate in bonds, such as in the planar and linear cases above, the polarisability of the central atom is smaller than when there are valence electrons not engaged in bonding. Lower polarisability favours larger bond angles. In addition, the ligands can add or withdraw electrons. For all molecules in the series examined, electrons are withdrawn from the central atom. SO$_3$ and SeO$_3$ illustrate this nicely. The bond angle in SO$_2$ and SeO$_2$ is just below 120°. Adding another oxygen atom removes further electron density from the central atom and the bond angle is increased. SO$_3$ and SeO$_3$ are planar molecules.

With the empirical confirmation presented in this section, that the bond angle decreases with higher polarisability of the centre atom, and that it increases with higher polarisability of the outer atoms, we turn in the next section to the discussion of the geometry of TTF whose off-planar geometry can also be understood in these terms.

4.7 The off-planar geometry of TTF

Now, consider also molecular bending in addition to the bond angle. It is not possible to draw resonant Lewis structures for the neutral TTF molecule. Would such structures exist, delocalisation energy could stabilise a planar geometry. In the absence of a stabilising delocalised $\pi$ system, why should TTF be planar? A boat shape fits best the experimentally observed electron diffraction patterns of TTF in the gas phase [70]. To show that the off-planar molecular geometry of TTF can be attributed to the polarisability of sulphur, the molecular geometry of TTF is compared with that of TOF and TSF. In these molecules, the sulphur atoms of TTF are replaced respectively by oxygen atoms (less polarisable) and selenium atoms (more polarisable). The molecular geometry of TOF is planar, TTF is boat-shaped and in TSF the molecular bending is more pronounced. The difference in geometry can be explained in terms of the C-X bond lengths and the $\theta_{C-X-C}$ bond angles in the series TXF, where $X \in \{O, S, Se\}$.

In Figure 30, a projection is presented where the three molecules are superimposed such that the four X atoms are in the xy plane. Note that the three C=C bonds are almost equal in length (1.30-1.32 Å) and that the main differences are the four C-X bond lengths and the $\theta_{C-X-C}$ angles inside each five-ring. The C-O, C-S, C-Se bond lengths are respectively 1.36 Å, 1.77 Å and 1.92 Å. The increase of the bond length can be seen as the increase of the size of the X atom, which clearly increases with larger polarisability. Consider a planar five-ring in TXF. Replacing O with S or Se, the bond length is increased and the ring angles adapt. The $\theta_{C-X-C}$ angles decrease in the planar TXF.
series as $105.0^\circ$, $95.0^\circ$, and $93.5^\circ$. Note that these values are close to the equivalent, unconstrained bond angles in $\text{H}_2\text{O}$, $\text{H}_2\text{S}$ and $\text{H}_2\text{Se}$ as obtained from HF calculations: $106.2^\circ$, $94.1^\circ$ and $93.1^\circ$, respectively. In the off-planar TTF and TSF molecules, where the angles are constrained in the five-rings, the $\theta_{C\times C}$ angles are only $0.2^\circ$ smaller than they are in a planar conformation. Apparently, the molecules can lower their energy by adopting smaller $\theta_{C\times C}$ angles and that is only possible when adopting an off-planar geometry. The $\theta_{C\times C\times C}$ dihedral angle, a measure of this off-planarity, becomes $9.2^\circ$ and $11.1^\circ$ in TTF and TSF respectively. The process that a reduction of too large bond angles in planar rings results in off-planar conformations is well understood. In the textbook case of cyclohexane, the $\theta_{C\times C\times C}$ bond angles reduce from $120^\circ$ in the planar conformation to $112^\circ$ (value from gas electron diffraction [22] is $111.4^\circ$) when adopting the chair conformation, lowering the total HF energy by 1.2 eV.

![Figure 30: Projection of optimised geometries (omitting Hs). From inside to outside: TOF, TTF and TSF.](image)

In 1997, Demiralp and Goddard [76] found TTF and TSF to be planar at the HF level of theory. They concluded that TTF adopts an off-planar geometry only when ring strain is introduced due to steric interactions by replacing the H atoms in TTF by bulky ligands such as F or Cl atoms or by $\text{CH}_3$ groups. We believe that the change in molecular bending can be fully rationalised by the Debye model. By analysing the atomic charges, the variations of the $\theta_{C\times C\times C}$ angles can be explained in these molecules. Whether this leads to a change in the off-planar molecular geometry depends on the other angles in the ring. When using the 6-31G** basis set for TTF, as Demiralp and Goddard did, and carefully choosing the start geometry we did find a boat-shaped geometry as the global minimum. When increasing the quality of the basis set by using ANO-S, the polarisability on S and Se becomes better modelled and the optimal bent geometries are easier to find in both TTF and TSF. MP2 results show an enhanced molecular bending of TTF: $\theta_{C\times X\times X\times C} = 19.4^\circ$ where Hargittai [70] determined it experimentally as $13.5^\circ$.

Upon ionisation, all TXF$^+$ molecules become planar. The $\theta_{C\times X\times C}$ angles increase by $0.5^\circ$ to $0.7^\circ$. It follows from charge analysis that the hole is predominantly located on the X atoms (about 40% for TOF$^+$, about 80% for TTF$^+$ and TSF$^+$) thereby reducing its polarisability. ESR measurements [52] confirm that the hole in TTF$^+$ is located mainly on the four S atoms. The reduction of polarisability in the series leads to a larger $\theta_{C\times X\times C}$ angle and planar ring geometry is favoured. The determination of the transition angle at which planarity commences is the subject of section 4.9. HF geometry optimisations of TTF and TSF, in which a chair conformation was used as a starting geometry, always led to boat-shaped conformations. Clearly the boat shape is favoured. When TTF and TSF are optimised with the constraint to remain planar, the bond lengths and angles essentially remain the same and the total energy is only a few meV higher. The small geometrical changes and the low energy involved in making the molecules planar show how delicate the balance is. In section 4.9, this is explored further in ring strain experiments in which the $\theta_{C\times X\times C}$ angle is varied. Now the TTF geometry is understood, the geometry of EDO-TTF is discussed in the next section.
4.8 The geometry of EDO-TTF

The molecular geometry of EDO-TTF is comparable to that of TTF with the difference that the bending in the ring with the attached EDO group is more pronounced. This is due to the electronegative EDO group. Analogous to the experiments in the previous section, EDO-TOF, EDO-TTF and EDO-TSF are used to study the effect of polarisability on molecule bending. Molecular bending is determined from the $\theta_{C-X-C}$ dihedral angles within a five-ring, as illustrated in Figure 31. The angle $\theta_2$ in the five-ring without the EDO group becomes larger within the molecular series. Comparing the geometry of EDO-TXF with that of TXF, the molecular bending angle $\theta_2$, the bond lengths and bond angles do not change appreciably. The result of adding the EDO group is a larger bending angle $\theta_2$ (analysed below). Moreover, there are other small differences in the geometry of the five-ring. Compared to their equivalents in TXF, the bond lengths are equal within 0.01 Å, and the bond angles within 3.3°. The most pronounced change is seen in the $\theta_{C-X-C}$ angles, which are reduced from 105.0°, 95.0° and 93.5° in the TXF series to 103.1°, 93.7° and 92.5° in EDO-TXF series. For a full table of bond angles and bond lengths of EDO-TXF we refer to Table 17 in appendix B. The other two angles in this five-ring, $\theta_{X-C-X}$ and $\theta_{C-C-X}$ become slightly larger (0.2°-1.4°) but they do not compensate the reduction of the $\theta_{C-X-C}$ angle. A decrease of the sum of the ring angles from 540° is a result, to 538.5° and 538.3°, respectively, in EDO-TTF and EDO-TSF and this is reflected in the larger bending angle $\theta_2$.

A Natural Bond Order (NBO) charge analysis based on the LoProp partitioning [111] shows that the predominant effect of adding the EDO group is that electrons are transferred from the doubly bounded carbon atoms of the five-ring, to which the EDO ring is attached, to the oxygen atoms of the EDO group. In fact, these oxygen atoms each adopt a charge -0.57 in EDO-TXF. The carbon atoms connected to the oxygen atoms of the EDO group supply approximately an equal amount of charge. The created positive charge on the carbon atoms of the five-ring is +0.27. The atomic charge for most of the other atoms in the molecule remains essentially the same.

Analysing further from the perspective of the $\theta_{C-X-C}$ bond angle, the effect of adding the EDO group can be summarised as follows. One carbon atom becomes more positive, while the charge of the other atoms remains the same. In the light of the Debye polarisability models, this extra positive charge is regarded as a decrease in atomic polarisability, which results in a decrease of the $\theta_{C-X-C}$ angle. That leads to a smaller sum of angles in the five-ring, which in turn leads to a larger molecular bending angle on the side of the molecule to which the EDO group is attached.

We end this section on EDO-TTF by discussing the optimum geometry of the neutral and ionised molecule in the context of our polarisability model. The geometries were optimised at the RHF level, UHF for EDO-TTF+, using the 6-31G** basis set [48] and the partial charges were obtained using the LoProp partitioning [111]. We analyse the geometry around sulphur atoms S₁ and S₂ in the two
five-membered rings, (Figure 32). Upon ionisation, the $\theta_{C-S-C}$ angles increase. This is explained as follows. The charge on the sulphur atoms decreases by 0.2, which we relate to a decrease in atomic polarisability $\alpha_S$. The charge on the carbon atoms remain almost the same, therefore $\alpha_C$ remains the same. Hence, the ratio between the polarisabilities, $\beta = \alpha_C/\alpha_S$, is increased and with that our model predicts a larger $\theta_{C-S-C}$ angle in the ionised molecule. The sum of the five angles in each ring becomes 540° and hence the molecular geometry becomes planar.

**Figure 32: Comparing the optimised geometries of neutral and ionised EDO-TTF.**

### Table 4.1

<table>
<thead>
<tr>
<th>Angle</th>
<th>EDO-TTF&lt;sup&gt;0&lt;/sup&gt;</th>
<th>EDO-TTF&lt;sup&gt;+&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_{C-S-C}$</td>
<td>95.0</td>
<td>95.5</td>
</tr>
<tr>
<td>$q_{C4}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$q_{S2}$</td>
<td>-0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$q_{C2}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\theta_{C1-S1-C3}$</td>
<td>93.7</td>
<td>95.1</td>
</tr>
<tr>
<td>$q_{C1}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$q_{S1}$</td>
<td>-0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$q_{C3}$</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

4.9 Determination of the transition angle $\theta_{C-X-C}$

The dependence of the molecular bending of neutral TXF on $\theta_{C-X-C}$ is determined by varying $\theta_{X-C-X}$, and by allowing the remainder of the system to relax in a HF geometry optimisation. In setting this angle, ring strain is introduced which is resolved when the other bonds and angles in the five-ring adjust. In this way, the $\theta_{C-X-C}$ angle, that determines the molecule bending, can be indirectly tuned. At the point where the molecular geometry becomes off-planar, the sum of the ring angles $\theta_{\text{total}} = \theta_{X-C-X} + 2(\theta_{C-C-X} + \theta_{C-X-C})$ deviates from 540° and a transition angle $\theta_{C-X-C, \text{transition}}$ can be determined.

It is observed in Figure 33 that for large $\theta_{X-C-X}$ the rings are planar with $\theta_{\text{total}} = 540°$. For small values of $\theta_{X-C-X}$ the molecules are boat-shaped and $\theta_{\text{total}} < 540°$. In the planar regime, all angles change linearly with $\theta_{X-C-X}$. In the non-planar regime, the change of the $\theta_{C-X-C}$ angle is not linear.

**Figure 33: Angles in the 5-ring (left axis) and $\theta_{\text{total}}$ (right axis) in dependence of $\theta_{X-C-X}$ (horizontal axis) in TOF, TTF and TSF. The vertical dashed line separates the planar and off-planar regimes. The arrow indicates $\theta_{X-C-X}$ in the fully optimised molecule.**

The transition angle, at which each molecule becomes bent ($\theta_{C-X-C, \text{transition}}$) is 109°, 95° and 93° in TOF, TTF and TSF respectively. The more polarisable atom X, the smaller the transition angle. The angle $\theta_{C-X-C}$ is clearly the weakest bond angle in the ring. When there is room in the ring for a smaller angle $\theta_{C-X-C}$ than the transition value, the molecule remains planar. When the other angles in the ring cause the angle $\theta_{C-X-C}$ to become larger than the transition value, the geometry of the rings change to non-planar and $\theta_{C-X-C}$ remains close to the value of $\theta_{C-X-C, \text{transition}}$. 
The procedure is repeated for ionised TXF. As mentioned in chapter 5, the electron is extracted predominantly from the four X atoms thereby reducing its atomic polarisability. The expectation from the Debye polarisability model is therefore that $\theta_{C-X-C}$ in TXF becomes larger on ionisation, and that therefore the transition angles should also increase. This is indeed the case. The transition angles $\theta_{C-X-C, \text{transition}}$ found are 123°, 106° and 102° in TOF+, TTF+ and TSF+, respectively.

In chapter 5, it is shown that the molecules become planar as soon as they are positively charged. Whether this also occurs on excitation is an interesting question. We speculate that, upon excitation, a bent molecule becomes planar. If this change in geometry can propagate to its neighbour molecule in the TTF stack, it could form the coherent phonon that is observed at the PIPT. This idea is supported by experiments by Lüer et al. [121] on (TMTTF)₂ dimers. They found that intermolecular bending and breathing modes are strongly coupled to the electronic transition.

4.10 Conclusions and discussion

The off-planar molecular geometry of EDO-TTF is explained using the extended Debye polarisability model. The molecular bending originates from the $\theta_{C-S-C}$ bond angles. These angles optimise to too small values for the five-rings in the molecule to remain planar. The extended Debye polarisability model gives a direct relation between the polarisability of sulphur and the bond angle.

We deduced the following rules:

1. the more polarisable the centre atom is, the smaller the bond angle becomes; and
2. the more polarisable the outer atoms are, the larger the bond angle becomes.

These relations were confirmed empirically with MP2 theory by optimising a set of A₂B and A₃B molecules and also by comparing the optimal HF geometry of TTF and EDO-TTF molecules with their selenium and oxygen substituted analogues. The molecules with oxygen substituents are planar whereas the selenium substituted molecules have a more pronounced molecular bending. The more pronounced bending of the ring with the EDO attachment in EDO-TTF is rationalised as follows. The EDO group withdraws electron density from the carbon atoms to which it is connected, thereby reducing the polarisability of these atoms. This reduces the $\theta_{C-S-C}$ angle which leads to more pronounced off-planar geometry of that five-ring. It is shown that there is a transition angle $\theta_{C-S-C, \text{transition}}$ at which the TTF molecule becomes off-planar, and that this angle depends on the polarisability at the sulphur atoms. By replacing S by O or Se the angle becomes respectively larger or smaller. Upon ionisation of the molecules, the transition angles increase due to the reduced polarisability of the central atom of the bond angle. The larger angle can be accommodated in the planar five-ring, hence TTF⁺ and EDO-TTF⁺ are planar.

We also obtained the molecular geometry of a series of other non-planar TTF derivatives. Their geometry is not further analysed and discussed but the optimised geometry is given in appendix D.

Elucidating the molecular geometry by using the extended Debye model provides a solid starting point for addressing the questions about the behaviour of the bulk material. We feel, it is the molecular geometry that plays a central role in the physics of the system. We recognise that whether or not the molecule is planar is directly coupled to the polarisability of the sulphur atoms. We have shown that a change in bond angle can be related to a change in polarisability, which in turn is correlated to a change in partial atomic charge.
In the past, Donald et al. [102] used similar expressions in models for the bond angle, which they termed polarised-ion models. These models were taken from work of Rittner [7], Hildenbrand [39] and DeKock et al. [61]. In their study on bond angles, bending forces and atomisation energies of group-2 and group-12 dihalides, bond angles were reproduced well whereas the calculation of forces and energies was more problematic. The group-12 dihalides proved to be beyond the capabilities of these classical models. The problems were ascribed to electron correlation and relativistic effects. As was shown in this chapter, by using the extended Debye model qualitatively, important general trends for the bond angle can be deduced and that these trends hold very well.