

Gap states in organic semiconductors: Hydrogen- and oxygen-induced states in pentacene

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First-principles pseudopotential density functional calculations are reported for hydrogen- and oxygen-related defects in crystalline pentacene ($C_{22}H_{14}$). It is shown that defects that perturb a carbon atom so as to remove its p_z orbital from participation in the π system give rise to a state in the gap. One such defect is formed by adding a H atom to create a $C_{22}H_{15}$ molecule with one fourfold C atom. In the neutral-charge state a single electron occupies a π orbital having reduced amplitude on the perturbed carbon atom. Charged defects correspond to addition or removal of an electron from this orbital. The possibility that these defects give rise to the bias-stress effect in pentacene-based thin film transistors is discussed.

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A large number of studies performed over the last several decades have focused on the structural and electronic properties of point defects in tetrahedrally coordinated inorganic semiconductors. As a result, the basic low-energy structural modifications (interstitials, vacancies, antisites) have been identified and transition levels in the band gap as well as formation energies within prescribed ranges of the atomic chemical potentials have been calculated.^{1,2} In comparison to research on inorganic semiconductors the identification and characterization of chemical defects in organic semiconductors is not a widely pursued activity and less is known about defects in those materials.³ This Rapid Communication presents models and calculations for chemical defects that give rise to localized gap states in pentacene, a prototype organic semiconductor. Of particular interest are those defects created by the addition of one or more H atoms to the pentacene molecules. And though the focus here is on pentacene, the underlying mechanism giving rise to the gap states is expected to be general and to apply to other small-molecule organic semiconductors as well as semiconducting polymers.

Pentacene ($C_{22}H_{14}$) is a planar molecule composed of five benzene rings fused along their sides, as shown in Fig. 1(a). To form the bulk triclinic crystal these molecules are arranged in a herringbone pattern with two molecules in each unit cell. Several different pentacene polytypes exist.⁴⁻⁶ They differ only slightly in their molecular packing and exhibit similar single-particle energy band gaps (1.9–2.2 eV).⁶

First-principles total-energy calculations have been performed for several types of defects. The first of these is formed by adding a H atom to the molecule to convert a C-H unit to a C-H₂ unit, thereby creating a $C_{22}H_{15}$ molecule, as depicted schematically in Fig. 1(b). In this type of defect, which will be denoted as a C-H₂ defect, one of the C atoms becomes fourfold coordinated and so does not participate in the π system. Also studied is the defect formed by replacing one of the H atoms by an oxygen atom, to create a $C_{22}H_{13}O$ molecule in which there is a C-O double bond. This will be denoted as an O_H defect. The calculations discussed below indicate that both of these defects will give rise to gap states in pentacene crystals.

Geometry-optimization and total-energy calculations⁷ were performed within the local density functional theory⁸ using first-principles pseudopotentials⁹ and a spin-

independent exchange-correlation energy functional.¹⁰ This approach was employed in recent calculations of the surface energies for polyacenes.¹¹ A plane-wave basis is employed with a cutoff energy of 50 Ry. Calculations have been performed for both isolated molecules and bulk systems. Calculations for defects in crystalline pentacene employed the triclinic lattice vectors determined by Campbell *et al.*⁵ using x-ray diffraction. The lattice vectors were kept fixed, but the internal coordinates of the atoms in the unit cell were allowed to relax. The resulting internal coordinates for bulk

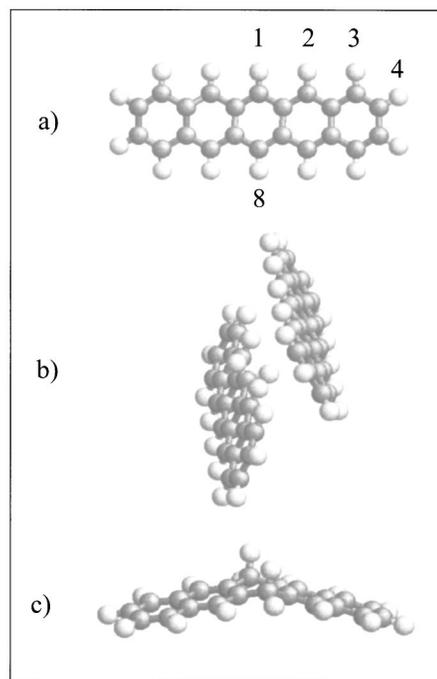


FIG. 1. (a) A single pentacene molecule ($C_{22}H_{14}$) consists of 5 benzene rings. In each molecule 14 of the 22 C atoms are bonded to two other C atoms and to one hydrogen atom. The four inequivalent H atoms are numbered 1–4. Other H atoms are related by symmetry. (b) A $C_{22}H_{15}$ molecule is shown next to a perfect pentacene molecule in crystalline pentacene. The added H atom is located in site 1. This is termed a C-H₂ defect. (c) A single $C_{22}H_{16}$ molecule (dihydropentacene) is shown here. The two C-H₂ units are positioned on sites 1 and 8.

pentacene are in good agreement with experiment.¹¹

Let us first consider an isolated pentacene molecule to which one additional H atom is added to create a $C_{22}H_{15}$ molecule. The H atom can be added on any one of four sites labeled 1–4 in Fig. 1(a). The most stable $C_{22}H_{15}$ molecule is formed by adding the H on site number 1, and additions on sites 2, 3, and 4 lead to structures that are higher in energy by 0.13, 0.64, and 0.72 eV. For the fourfold C atom to achieve tetrahedral coordination a distortion of the molecule is required. This results in a nonplanar $C_{22}H_{15}$ molecule. However, the energy difference between planar and nonplanar configurations of the isolated $C_{22}H_{15}$ molecules is less than 0.02 eV/molecule. For the $C_{22}H_{13}O$ molecules, formed by replacing a H atom by an oxygen atom on one of the four sites, a very similar trend in the relative energies is obtained. Substitution on site 1 results in the most stable structure. Substitution on sites 2, 3, and 4 results in structures higher in energy by 0.11, 0.55, and 0.72 eV. The similarity in the position dependence of the defect creation energies for the $C_{22}H_{15}$ and $C_{22}H_{13}O$ molecules is a consequence of the fact that the π bonding is perturbed in the same way in each case: In both systems the p_z orbital on the perturbed C atom no longer participates in the π system once the defect is present. This is clear in the case of the $C_{22}H_{15}$ molecule where the perturbed C atom becomes fourfold coordinated. For the $C_{22}H_{13}O$ molecule a strong double bond is formed between the O and C atom, and this effectively decouples this C p_z orbital from the molecular π system. The gap-state wave functions for the $C_{22}H_{15}$ and $C_{22}H_{13}O$ molecules are shown in Fig. 2. We will refer to these states as π -gap states since they have π character and reside within the highest occupied and lowest unoccupied molecular orbital (HOMO-LUMO) gap of the unperturbed pentacene molecule. It is seen that these two orbitals are very similar in character and that the p_z orbitals of the perturbed C atoms do not participate in either state. One may view these π -gap states as superpositions of occupied π and empty π^* orbitals of the perfect molecule; this combination of orbitals produces a node on the perturbed C atom.¹² Such π -gap states are therefore expected to be a characteristic feature of defects in organic semiconductors in which a C p_z orbital is removed from the π system.

The C-H₂ defect is a representative of the class of defects in which the defining characteristic is the removal of a C p_z orbital from the π system. Another member of this class is formed by attaching an OH group to a C atom to create a $C_{22}H_{15}O$ molecule. In this defect, which may be termed C-HOH, a C atom becomes fourfold coordinated and its p_z orbital is removed from the π system. Calculations for an isolated $C_{22}H_{15}O$ molecule confirm the presence of a π -gap state of character similar to those shown in Fig. 2 for the $C_{22}H_{15}$ and $C_{22}H_{13}O$ molecules. Consequently, the presence of $C_{22}H_{15}O$ molecules in bulk pentacene is expected to give rise to electrically active gap states. There have been some recent experimental studies¹³ of pentacene in which deep levels were attributed to the presence of oxygen, but no specific structural models for the defects were proposed. Organic semiconductor device characteristics are known to be sensitive to air exposure. Indeed, pentacene thin-film transis-

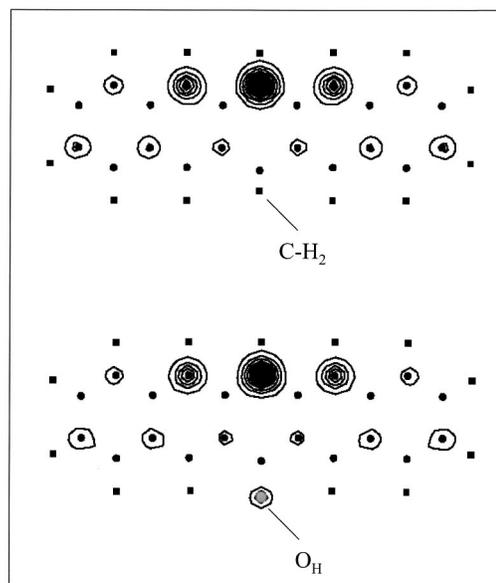


FIG. 2. Contour plots of the π -gap wave functions for $C_{22}H_{15}$ (top) and $C_{22}H_{13}O$ (bottom). In each case the plane of the plot is located 1 bohr above the plane of the molecule. Atom positions (projected onto this plane) are indicated. C atoms are denoted by solid circles. The H atoms are denoted by solid squares. In projection, the H atoms in the C-H₂ unit in site 1 appear closer to the C. The O atom in site 1 is denoted by a gray circle. Note that in both orbitals there is very little weight on the perturbed C atom. In the neutral-charge state these orbitals would be occupied by a single electron and there is a net spin. Because the spin density is spread out over the entire molecule, the spin-polarization energy is expected to be small, on the order of 0.1 eV.

tors may be employed as sensors of humidity.¹⁴ It is therefore worth noting that dissociation of H₂O may give rise to both C-H₂ and C-HOH defects, and it is possible that the formation of these defects affects the properties of such devices upon exposure to humid air.

Calculations have also been performed for isolated molecules containing two C-H₂ defects: i.e., dihydropentacene ($C_{22}H_{16}$). A variety of possible structures were considered, and the lowest-energy structure obtained is one in which the two C-H₂ defects are located on sites 1 and 8. In the lowest-energy configuration the molecule is folded by 28° as shown in Fig. 1(c). This distortion lowers the energy by 0.11 eV/molecule compared to a structure having mirror symmetry in the plane. This energy reduction is quite small, and the interactions between the impurity and neighboring pentacene molecules make it unlikely that such a large distortion would persist when the molecule is embedded as a dilute impurity in crystalline pentacene. Therefore, in the calculations of defect formation energies in crystalline pentacene discussed below, a symmetric dihydropentacene impurity molecule is employed.

We now turn to the calculations performed for defects in crystalline pentacene. The defects are modeled with a triclinic unit cell containing two molecules in each cell, one defect molecule and one $C_{22}H_{14}$ molecule. The formation energies of the C-H₂ defect ($C_{22}H_{15}$), the dangling bond

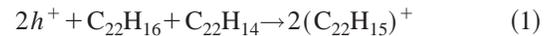
defect ($C_{22}H_{13}$), and the dihydropentacene defect ($C_{22}H_{16}$) are determined with respect to bulk pentacene and a reservoir of H with chemical potential (μ_H). Neglecting corrections arising from changes in the zero-point vibrational energies,¹⁵ the formation energy of the neutral C-H₂ defect is $\Omega(\mu_H) = -0.2 \text{ eV} - \Delta\mu_H$. In this expression, $\Delta\mu_H = \mu_H - \frac{1}{2}E(H_2)$ and $E(H_2)$ is the energy of a H₂ molecule at rest in the vacuum. According to this result, it is exothermic by a small amount to move H from a H₂ molecule to form the C-H₂ defect in bulk pentacene. The formation energy of dihydropentacene is $\Omega(\mu_H) = -1.4 \text{ eV} - 2\Delta\mu_H$. Therefore, when the zero-point energy correction is included the predicted exothermicity of the reaction $C_{22}H_{14} + H_2 \rightarrow C_{22}H_{16}$ is $\sim 1.1 \text{ eV}$. For the dangling bond defect the formation energy is $\Omega(\mu_H) = 3.5 \text{ eV} + \Delta\mu_H$: i.e., it costs 3.5 eV per H atom to remove H from pentacene and form H₂ molecules in the vacuum. It is clear from these formation energies that reactions leading to the addition of H are more likely than those leading to loss of H. It is also important to note that for pentacene depositions that are performed using a H₂ carrier gas at temperatures and pressures such that $2\Delta\mu_H$ is greater than -1 eV , one can expect (to the extent that equilibration between pentacene and molecular hydrogen can be assumed) a significant quantity of dihydropentacene in the resulting material. For a carrier gas pressure of 1 atm this condition on $2\Delta\mu_H$ is met for temperatures up to about 400 °C.¹⁶

For the C-H₂ and O_H defects positive- and negative-charged states are formed by the removal or addition of an electron from the π -gap states. The transition levels are values of the electron chemical potential (E_F) for which the energies of defects having different charge states are equal.^{1,2} The calculated (+/0) level for the C-H₂ defect occurs at about 0.34 eV above the valence-band maximum and the (0/-) level occurs at about 0.80 eV. Thus the neutral defect is stable over a 0.5-eV-wide range of the electron chemical potential. It may therefore be of interest to perform electron-spin-resonance experiments on hydrogenated pentacene or other hydrogenated organic semiconductors. The corresponding transition levels for the O_H defect are located at 0.18 and 0.62 eV relative to the valence-band maximum. The formation of C-H₂ and O_H defects may act as compensation mechanisms for both *p*- and *n*-type doping. In each case the formation energy is reduced, and hence the number of such electrically active defects increases as the electron chemical potential moves towards the band edges.

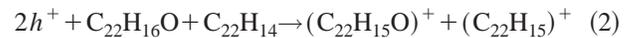
The energy of the structure with paired C-H₂ defects may be compared with that in which the two neutral C-H₂ defects are located on separate molecules in the crystal, and it is found that it is energetically favorable for C-H₂ defects to be located on the same molecule. The energy reduction arising from this pairing of neutral defects is $E_{pn} = 1.04 \text{ eV}$. (The corresponding pairing energy obtained in calculations for isolated molecules is 1.13 eV.) Because the HOMO and LUMO for the $C_{22}H_{16}$ molecule lie below and above those for the perfect molecule, molecules having a 1-8 pair of C-H₂ units are not electrically active, and so most of the extra H will not give rise to gap states. The pairing energy depends on the charge state of the unpaired C-H₂ defects

and, hence, depends on the Fermi energy. In *p*-type conditions $E_p(E_F) = E_{pn} + 2[E_F - E(+/0)]$ and in *n*-type conditions $E_p(E_F) = E_{pn} - 2[E_F - E(0/-)]$ so that when E_F is below the (+/0) transition level or above the (0/-) level the energy cost of breaking a pair is reduced.

We may employ these results to discuss the possibility that the formation of charged C-H₂ defects is related to the bias-stress effect observed in pentacene and other organic semiconductors.^{17,18} According to Knipp *et al.*, the threshold voltage shifts seen in pentacene thin-film transistors following the application of a gate bias stress can be accounted for by the accumulation of charge at the interface between pentacene and the dielectric. The magnitude of the shift requires that the interface state density created by the stress be on the order of $10^{12}/\text{cm}^2$ (Ref. 17). The reactions



and



lead to hole trapping and the formation of charged defects. In principle, these reactions can give rise to charge at the interface. As discussed above, the reaction energy depends on the electron chemical potential (E_F) and is reduced as E_F moves towards the band edge. The first reaction proceeds by transferring a proton from one molecule to a neighbor, thereby creating two charged C-H₂ defects and removing two holes. This hydrogen abstraction reaction, which is a common reaction of positively charged hydrocarbon molecules,¹⁹ is relevant when there is an excess of H in the system. Most of this excess H is normally paired and hence electrically inactive, but application of a field and the reduction of the Fermi level drives the reaction to the right. In the second reaction a proton is transferred from a $C_{22}H_{16}O$ molecule to a neighboring pentacene molecule. Threshold shifts were seen for both positive and negative gate voltages, implying that both negatively and positively charged defects can be created by the stress.¹⁷ In this context it is noted that electron trapping can give rise to negatively charged $C_{22}H_{15}$ molecules under *n*-type conditions.

One may employ the law of mass action to estimate the fraction (*S*) of pentacene molecules on which a single C-H₂ unit is present if a fraction (*P*) of the molecules have a pair of C-H₂ units present. Under equilibrium conditions at temperature *T*,

$$S = P^{1/2} \exp[-E_p(E_F)/2k_B T].$$

When a large concentration of holes is present, E_F is shifted to the valence-band edge, $E_F = 0$. With $E(+/0) = 0.34 \text{ eV}$ one then finds $E_p(E_F) \sim 0.36 \text{ eV}$, and so for a temperature $T \sim 300 \text{ K}$ the result is $S \sim 10^{-3} P^{1/2}$.

The density of pentacene molecules in a single layer is $4 \times 10^{14}/\text{cm}^2$. It is reasonable to assume the interface charge is spread over several layers, so that the effective molecular density is $\sim 10^{15}/\text{cm}^2$. Therefore, the scenario in which a charge density of $10^{12}/\text{cm}^2$ results from the thermal creation of charged C-H₂ defects under *p*-type conditions requires $P > 0.1$. This result suggests that a significant fraction of

$C_{22}H_{16}$ molecules must be present in the pentacene to account for the effect. This conclusion is qualitative because an uncertainty in the pair breaking energy, $E_p(E_F)$, as small as 0.1 eV translates into an uncertainty in S of almost a factor of 10. Nonetheless, it is clear that a field-induced creation of charged $C_{22}H_{15}$ molecules should be considered as a possible mechanism producing bias stress in pentacene. Experimental evidence for the existence of $C_{22}H_{16}$ in pentacene has been obtained recently.^{20,21} In addition, the possible presence of $C_{22}H_{16}$ can be inferred from analysis of the chemical precursors that are employed in the synthesis of pentacene.²²

In summary, it has been proposed that electrically active gap states will be a characteristic feature of C-H₂, O_H, and C-HOH defects in organic semiconductors because these defects remove a C p_z orbital from the π system. It was shown that C-H₂ defects prefer to form pairs (i.e., $C_{22}H_{16}$ molecules) and that the energy required to break these pairs depends on the Fermi level. It is possible that the breaking of these pairs and the formation of charged defects gives rise to the bias-stress effect observed in pentacene.

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