Synthesis and Combined Experimental and Theoretical Characterization of Dihydro-tetraaza-acenes

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ABSTRACT: We present a combined experimental and theoretical study of electronic and optical properties of dihydro-tetraaza-acenes (DHTAₙ). Using solvent-free condensation, we are able to synthesize not only DHTA5 but also the longer DHTA6 and DHTA7 molecules. We then investigate their gas-phase electronic structures by means of ab initio density functional calculations employing an optimally tuned range-separated hybrid functional. By comparing with the parent linear oligoacenes (nA) and based on computed ionization potentials and electron affinities, we predict DHTAₙ molecules to be more stable than acenes of the same length, where we expect DHTAₙ molecules to be persistent at least up to n = 7 rings. We further exploit the analogy with nA by analyzing the entire intramolecular π-band structure of the DHTAₙ molecules. This clearly reveals that the additional two electrons donated by the dihydropyrazine group are delocalized over the entire molecule and contribute to its π-electron system. As a consequence, the symmetry of the frontier orbitals of DHTAₙ differs from that of the parent nA molecule. This also affects the UV−vis absorption spectra which have been measured for DHTA5, 6, and 7 dissolved in dimethyl sulfoxide and analyzed by means of excited state calculations within a time-dependent density functional theory framework.

INTRODUCTION

In the field of organic electronics, pentacene (5A) is presumably one of the most investigated organic molecules covered by a vast literature ranging from device physics over to fundamental studies on electronic and optical properties. However, pentacene suffers from long-term stability issues because of its photo-oxidation and low thermal stability. To overcome these limitations and to provide alternative molecules with improved film morphology and stability, nitrogen-containing derivatives of pentacene, N-heteroacenes, have been shown to be promising. The synthesis of larger heteroacenes and the investigation of their properties have already a long-standing history. As early as in 1901, Hinsberg has presented a comprehensive investigation of such multunit nitrogencontaining ring systems, thereby discovering interesting properties regarding their chemical stability or fluorescence properties. In the 1960s, Kummer and Zimmermann have systematically studied the electronic properties of linear diaza- and tetra-azacenes compared with that of the parent oligoacenes. More recently, Nuckolls and co-workers have demonstrated the fabrication of a thin-film transistor based on a hydrogenated diaza-pentacene, whereas Winkler and Houk have discussed the usage of nitrogen-rich oligoacenes as n-channel transistors based on density functional calculations.

We decided to focus on 5,14-dihydro-5,7,12,14-tetraazapentacene derivatives (DHTAₙ) depicted in Scheme 1 because of two fundamental features inherent to their chemical structure which offer a number of opportunities to manipulate and control the electronic properties, the stability, and the supramolecular arrangement in the solid. First, these N-heteroacenes can be viewed as constituted of dihydropyrazine units which add two more electrons to the π-system and provide a number of additional opportunities to manipulate and control their electronic and optical properties.
thereby stabilize the molecule.23 Second, the presence of H-donor (dihydropyrazine, N–H) and H-acceptor sites (pyrazine, N) leads to well-organized intermolecular H-bonding networks, forming a stable arrangement in the solid state.24 The first documented molecule of that sort, 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAS), has in fact been synthesized as early as 189025 and also been investigated in the seminal work by Hinsberg who called this molecule homofluorindin.20 Its structural and electrochemical properties have already been reported24,25,27 and its electronic band structure has been revealed by ultraviolet photoemission spectroscopy.26 Driven by new efficient synthesis routes,22 its fundamental properties and its potential for organic devices have been assessed.17,18,23,29–31 However, extended DHTAn for \( n > 5 \) have not been reported so far where the presence of extra phenyl rings should affect the stability of their oxidized and/or reduced forms. Also, a systematic study on the electronic structure of the whole DHTAn family of molecules using a state-of-the-art and predictive ab initio electronic structure method is still lacking.

In this work, extended DHTAn have been synthesized \((n = 6, 7)\) and fully characterized. Using a combined experimental and theoretical approach, we investigate their electronic and optical properties. Theoretically, we perform density functional theory (DFT) calculations for the gas-phase oligoacene \((\text{DFT})\) calculations for their electronic and optical properties. Theoretically, we perform density functional theory (DFT) calculations for the gas-phase oligoacene \((\text{DFT})\), has in fact been synthesized as early as 1890 and also been investigated in the seminal work by Hinsberg who called this molecule homofluorindin. Its structural and electrochemical properties have already been reported and its electronic band structure has been revealed by ultraviolet photoemission spectroscopy. Driven by new efficient synthesis routes, its fundamental properties and its potential for organic devices have been assessed. However, extended DHTAn for \( n > 5 \) have not been reported so far where the presence of extra phenyl rings should affect the stability of their oxidized and/or reduced forms. Also, a systematic study on the electronic structure of the whole DHTAn family of molecules using a state-of-the-art and predictive ab initio electronic structure method is still lacking.

In this work, extended DHTAn have been synthesized \((n = 6, 7)\) and fully characterized. Using a combined experimental and theoretical approach, we investigate their electronic and optical properties. Theoretically, we perform density functional theory (DFT) calculations for the gas-phase oligoacene \((\text{DFT})\) and dihydro-tetraaza-acene \((\text{DHTAn})\) molecules. In addition to a standard exchange–correlation functional, a generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE),32 we employ a range-separated hybrid (RSH) density functional, with an asymptotically exact long- and short-range fractional Fock exchange, where the parameters are tuned nonempirically, per system, on the basis of exact physical constraints, also known as optimally tuned RSH (OT-RSH).33–35 This method leads to highly reliable values for the ionization potentials (IPs) and the electron affinities (EAs) for DHTAn which we compare to the parent \( n \text{A} \) series. Moreover, we also present a comparison of the \( n \) bands of DHTAn with those of \( n \text{A} \) with an emphasis on the changes induced by the pyrazine and dihydropyrazine groups. We envision that the insights gained by our study will be not only important for further exploiting DHTAn molecules for various applications but also useful for designing other novel N-heteroacenes.

**METHODS**

**EXPERIMENTAL SECTION**

**Synthesis and Characterization of DHTA6.** A well-mixed solid of phenazine-2,3-diol \((m = 800 \text{ mg}, 3.72 \text{ mmol}, 1 \text{ equiv})\), 2,3-diaminonaphthalene \((m = 626 \text{ mg}, 3.96 \text{ mmol}, 1.05 \text{ equiv})\), and benzoic acid \((m = 4.9 \text{ g}, 40.0 \text{ mmol}, 10 \text{ equiv})\) was heated to 400 °C for 10 min. Then, EtOH was added to the hot mixture. This dark-colored suspension in EtOH \((v = 50 \text{ mL})\) was sonicated \((\text{60 °C}, 1 \text{ h})\), filtrated, and washed with dimethyl sulfoxide (DMSO) and acetone. The desired product was afforded after 3 times sublimations under vacuum \((8 \text{ mbar}, 450 °C\) for \(15 \text{ min}\)).

**METHODS**

**EXPERIMENTAL SECTION**

**Synthesis and Characterization of DHTA7.** A well-mixed solid of 2,5-dihydroxy-1,4-benzoquinone \((m = 445 \text{ mg}, 3.18 \text{ mmol}, 1 \text{ equiv})\), 2,3-diaminonaphthalene \((m = 1020 \text{ mg}, 6.45 \text{ mmol}, 2.03 \text{ equiv})\), and benzoic acid \((m = 7.2 \text{ g}, 59.0 \text{ mmol}, 18 \text{ equiv})\) was heated to 360 °C for 15 min. Then, EtOH was added to the hot mixture. This dark-colored suspension in EtOH \((v = 50 \text{ mL})\) was sonicated \((60 °C\) for \(1 \text{ h})\) and filtrated thrice. The desired product was afforded after 3 times sublimations under vacuum \((8 \text{ mbar}, 450 °C\) for \(15 \text{ min}\)).

**Computational Details.** Within the generalized Kohn–Sham formalism, RSH functionals consist of a partition of the Coulomb interaction as

\[
\frac{1}{r} = \frac{\alpha + \beta \epsilon(r/r)}{r} + \frac{1 - (\alpha + \beta \epsilon(r/r))}{r}
\]

Here, \( r \) is the interelectron coordinate, \( \epsilon \) is the error function, and \( \alpha, \beta, \gamma \) are parameters, which in principle may be freely chosen or determined empirically.38 The first term in eq 1 is treated within Hartree–Fock (HF) theory, while the second one is treated within a standard semilocal \( \text{ HF} \) approximation.31 The range-separation parameter \( \gamma \) controls which of the two terms dominate at a given distance. It has been repeatedly shown that \( \gamma \) can be strongly system- and size-dependent,33,35,42–44 thus, one uniform value for \( \gamma \) is not sufficient. Therefore, we prefer to determine it separately for each system by enforcing a nonempirical condition: we make use of the IP theorem43–46 and choose \( \gamma \) such that the difference between the energy of the highest occupied molecular orbital (HOMO) level and the IP is minimized. Specifically, this is accomplished by minimizing the following target function

\[
J^2(\gamma; \alpha) = \sum_i \left[ \epsilon_{\text{H}(N+i)}^{\alpha} + \text{IP}^{\alpha}(N + i) \right]^2
\]

Here, the \( \epsilon_{\text{H}(N+i)}^{\alpha} \) are the HOMOs of the \((N + i)\) electron molecular systems and \( i \) is an integer number. The \( \text{IP}^{\alpha}(N + i) \) are the corresponding IPs, which are calculated from the total energy difference between the \((N + i)\) electron and the \(N + i\) electron system. In eq 2, when \( i = 0 \), the HOMO of the neutral system is adjusted with the IP, whereas when \( i = 1 \), the IP of the anionic system, that is, the EA of the neutral system, is considered, such that its difference from the lowest unoccupied molecular orbital (LUMO) eigenvalue is minimized.35 Note that \( \gamma \) has to be tuned for each choice of \( \alpha \) separately.

As can be seen from eq 1, the parameters \( \alpha \) and \( \beta \) control the behavior of the Fock term for \( r \to 0 \) and \( r \to \infty \), leading to \( \frac{1}{r} \) and \( \frac{1}{r^2} \), respectively. The asymptotic behavior of the \( \alpha \) functional for \( r \to \infty \) has been shown to be crucial for obtaining accurate HOMO–LUMO gaps and thereby introduces another constraint on the parameters. For a gas-phase molecule, enforcing \( \alpha + \beta = 1 \) leads to the correct \( \frac{1}{\sqrt{r}} \) asymptotic behavior.39 As a consequence, the semilocal contribution in the long range vanishes and \( \alpha \) controls the amount of nonlocal Fock exchange in the short range.

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be seen in the expression for the exchange–correlation energy of the RSH functional, obtained with this constraint\textsuperscript{34}

\[ E_{xc} = (1 - \alpha)E_{xc}^{SR} + \alpha E_{xc}^{HF} + E_{xc}^{LR} + E_{xc}^{SL} \]

(3)

where \( E_{xc}^{SR} \) and \( E_{xc}^{SL} \) denote semilocal exchange and correlation, respectively, and \( E_{xc}^{HF} \) denotes nonlocal Fock exchange.

We have also simulated the optical absorption spectrum of molecules in solution. To this end, we have taken into account the dielectric constant of the solvent, DMSO, for which we take an experimental literature value of \( \varepsilon = 2.18 \). Enforcing the correct asymptotic behavior of the exchange potential in the solvent, \( \frac{1}{\varepsilon} \) requires to choose \( \alpha + \beta = \frac{1}{2} \). Thus, the exchange–correlation energy is generalized to

\[ E_{xc} = (1 - \alpha)E_{xc}^{SR} + \alpha E_{xc}^{SR} + \left( 1 - \frac{1}{\varepsilon} \right)E_{xc}^{LR} + \frac{1}{\varepsilon}E_{xc}^{LR} + E_{xc}^{SL} \]

(4)

Note that eq 4 reduces to eq 3 in the gas-phase case where \( \varepsilon = 1 \). Using the functional form of eq 4, we have computed the spin-restricted vertical excitation energies within the framework of time-dependent DFT (TD-DFT) using the Casida formalism.\textsuperscript{50}

All electronic structure calculations have been performed using the \textit{ab initio} computational chemistry software package NWChem.\textsuperscript{51} The Gaussian-based DFT module has been used with a cc-PVTZ basis set. For the computations, we have utilized the standard PBE exchange–correlation functional\textsuperscript{33} as well as the long-range-corrected RSH functional (LC-wPBE). Note that the preceding geometry relaxations have been performed using the PBE functional and all molecular geometries are found to be planar.

**RESULTS**

**Synthesis.** DHTA5 was prepared according to the procedure reported in the literature\textsuperscript{24} using solvent-free condensation between the commercially available 2,5-dihydroxy-p-benzoquinone 1 and o-diaminobenzene 2 (2 equiv) (Scheme 2). This reaction occurs at high temperature in the presence of excess PhCO\textsubscript{2}H as the catalyst to afford the target pentacycle that could be easily isolated by filtration in 80% yield. DHTA6 could be isolated as a violet solid in 58% yield by reacting similarly the commercially available 2,3-diaminonaphthalene 4 and 2,3-dihydroxyphenazine 3, which could be obtained in a previous work from 1 and 2 (1 equiv).\textsuperscript{24} The same procedure using precursors 1 and 4 (2 equiv) leads to the formation of DHTA7 in 61% yield (see the Experimental Section).

**Influence of Short-Range Exchange.** For our gas-phase DFT calculations, we have tuned the range-separation parameter \( \gamma \) by minimizing the target function defined in eq 2 by taking into account, both, the neutral molecule (\( i = 0 \)) and the anion (\( i = 1 \)). To judge the influence of \( \alpha \), the fraction of short-range HF exchange, on the orbital energies, we have varied \( \alpha \) from 0 to 0.5 and optimally tuned \( \gamma \) for each value of \( \alpha \). The results for DHTA5 are plotted in Figure 1. First, we notice that compared to the GGA-PBE result of 1.77 eV, the HOMO–LUMO gap is considerably widened to 5.60 eV in a symmetric manner. The OT-RSH value of the gap, in fact also insensitive to the value of \( \alpha \). This is because the IP and the EA are mainly governed by the asymptotic behavior of the respective orbital that depends on the long-range behavior of the exchange–correlation potential which is independent of \( \alpha \). As expected, the optimal range-separation parameter \( \gamma_{opt} \) reduces with increasing \( \alpha \). Such a behavior can be rationalized because the range \( 1/\gamma_{opt} \) at which full Fock exchange sets in can be extended to larger distances if the amount of the Fock exchange at short range, governed by \( \alpha \), is increased.\textsuperscript{34,36}

We have color-coded the orbital energies according to the symmetry of the respective orbitals that are depicted in panel (b) of Figure 1. All \( \pi \) orbitals with no node in the \( x_z \)-plane, denoted as \( \pi_{m,0} \), and the respective orbital energies are plotted in red, while \( \pi \) orbitals with a node in the \( x_z \)-plane, denoted as \( \pi_{m,1} \) are plotted in orange. Here, \( m \) counts the nodes along the long molecular axis (\( x \)-axis). Orbitals of \( \sigma \) symmetry are shown in green, specifically two states denoted as \( \sigma_{s} \) and \( \sigma_{t} \), which are centered around the pyrazine groups of the molecule. In contrast to the \( \pi \) states, these orbitals exhibit a pronounced dependence on the amount of short-range HF exchange. This is the typical behavior for comparably localized states resulting from the growing compensation of the self-interaction error with increasing \( \alpha \).\textsuperscript{36} Note that for the remaining part of the paper, we have set \( \alpha = 0.25 \) because this value has been shown to yield the best agreement with quasiparticle calculations for...
other pentacene derivatives as well as for the organic pigment PTCDA.

It is worth mentioning that the two types of π orbitals introduced in Figure 1, namely, π6,0 and πm,1, are sometimes also termed linking and apex π bands, respectively, referring to the position of the carbon atoms with the strongest contribution. For instance, the HOMO of DHTAS, denoted as π6,0, has six nodes along the long molecular axis and it belongs to the linking band. Interestingly, the HOMO of DHTAS has the same nodal structure as the LUMO of pentacene. This is because DHTAS has two π electrons more compared to pentacene owing to the two N−H groups which each contribute one more π electron. Thus, overall DHTAS exhibits 24 π electrons which lead to 12 occupied states, 5 of which are in the apex band (π0,1, π1,1, ..., π3,1) and 7 in the linking band (π6,0, π3,0, ..., π0,0).

**Frontier Orbitals.** Naively, one may conclude that 24 π electrons for DHTAS, as compared to 22 π electrons for 5A, may destabilize DHTAS relative to 5A following the so-called π Huckel rule. This is, however, not the case as can be seen from a comparison of the frontier orbitals, that is, the HOMO and LUMO energies, between DHTAn and the parent nA molecules which is the focus of this subsection.

In Figure 2, we have depicted the IP and the EA, computed from the OT-RSH functional with 0.25 for oligoacenes from naphthalene (n = 2) up to heptacene (n = 7) as black triangles and for the DHTAn for n = 5, 6, 7, 9, 11 as red circles. For the oligoacenes up to pentacene, we have also included experimental data (blue plus signs) for the IP and the EA. Both, experiment and calculation, nicely show the reduction of the IP and the increase in EA, respectively, in the series from naphthalene (n = 2), anthracene (n = 3), tetracene (n = 4), and pentacene (n = 5). The OT-RSH results slightly underestimate IP with a maximum deviation of 0.3 eV compared to the experiment, while the EA values all agree within ±0.15 eV. The further decrease in IP (increase in EA) computed for hexacene (n = 6) and heptacene (n = 7) is in fact the reason for the well-known chemical instability of linear acenes longer than pentacene.

We now turn to the OT-RSH results for the DHTAn molecules represented as red circles in Figure 2a. When comparing nA with DHTAn of the same length, we clearly observe a stabilization of, both, the IP and the EA. For instance, for n = 5, the IP increases by 0.3 eV and the EA reduces by almost 0.5 eV because of the introduction of the pyrazine and dihydro.pyrazine groups. We predict that this trend is continued for the longer molecules such that one can expect chemically stable dihydro-tetraaza-acenes up to 7 rings. While our computed EA for DHTAn has the expected trend as a function of n, we observe a peculiar behavior of the IP for which the OT-RSH results predict an almost constant value of 6.6 eV between n = 5 and n = 7 before it considerably reduces for n = 9 and n = 11. We believe that this is related to the underlying structure of the π bands of linear oligoacenes which will be the focus of the next subsection.

Before we close this section, we briefly point out that, as depicted in panel (b) of Figure 2, the optimal range-separation parameter γopt also follows a clear trend as a function of the molecular length n, where almost the same values for nA and DHTAn have been computed. The longer the molecule, the smaller γopt has to be chosen; in other words, the larger the distance dividing the short from the long range, 1/γopt has to be chosen. Interestingly, we find a linear trend as a function of the inverse length n with a saturation value of γopt = 0.07 bohr for a hypothetical infinitely long acene chain.

**π Bands.** For pentacene, it has been shown that the orbital energies of the 11 occupied π orbitals can be interpreted as intramolecular band structure grouped into the linking band containing six and the apex band containing five orbitals, respectively. This intramolecular band structure could also be measured by means of angle-resolved photoemission spectroscopy (ARPES). Here, we show that the π orbitals of dihydro-tetraaza-acenes strongly resemble those of the parent oligoacenes and can be equally represented as the intramolecular band structure.

Clearly, to establish an intramolecular energy dispersion relation, orbital energy E versus momentum k, a momentum value k needs to be assigned to a given orbital. Now, for a molecule of finite length, the momentum k is not a good quantum number. For molecules with a quasiperiodicity such as nA and DHTAn, we can nevertheless define a quasimomentum value by computing the Fourier transform of the orbital and assigning the k-value to the maximum intensity in Fourier space. Such theoretical momentum maps are depicted in Figure 3a for the LUMO + 1, LUMO, and HOMO of SA (top to bottom) and in Figure 3b for the LUMO, HOMO, and HOMO − 1 of DHTAS, respectively, where the k-values corresponding to the maximum intensity in momentum space are indicated by the vertical dashed lines. It should be noted that the theoretical momentum maps for SA have already been experimentally confirmed by analyzing the photoelectron...
Figure 3. (a) Theoretical momentum maps of the LUMO + 1 ($\pi_{6,0}$), LUMO ($\pi_{5,0}$), and HOMO ($\pi_{4,1}$) of SA with the $k_x$-value at maximum intensity indicated as vertical dashed lines. (b) Same as (a) for the LUMO ($\pi_{5,0}$), HOMO ($\pi_{6,0}$), and HOMO − 1 ($\pi_{5,1}$) of DHTA5. (c) Orbital energies of nA and DHTA molecules plotted vs the respective $k_x$-value defined in panel (a). Filled and open symbols correspond to the linking and apex $\pi$ bands denoted as $\pi_{m,0}$ and $\pi_{m,1}$, respectively. The solid and dashed black lines correspond to the $\pi$-band structure of a hypothetical infinite polycyclic chain, where empty bands (dashed lines) have been rigidly shifted to match the empty orbitals of the acenes.

angular distribution within ARPES experiments.\textsuperscript{52,53,56--58} Using the technique of photoemission tomography,\textsuperscript{59} such measurements are being planned also for DHTA in future.

As already mentioned earlier, the LUMO and HOMO belong to the linking band with seven and six nodes perpendicular to the long axis, respectively, and no nodal plane parallel to the long molecular axis. Roughly speaking, given the length of DHTA\textsubscript{5}, $L \approx 12.1$ Å, the $k_x$-values are simply determined by $k_{n} = \pi L/m$, where $m$ is the number of nodes. This leads to 1.55 and 1.82 Å\textsuperscript{-1} for the HOMO ($\pi_{6,0}$) and LUMO ($\pi_{5,0}$), respectively, while the more precise values determined from the momentum maps, from which also the momentum spread $\Delta k$ is apparent, are 1.51 and 1.70 Å\textsuperscript{-1}. Similarly, the HOMO − 1 ($\pi_{5,1}$) would be assigned a $k_x$-value of 1.04 Å\textsuperscript{-1} from simple node counting arguments, while the momentum map yields 1.18 Å\textsuperscript{-1}.

When plotting the computed orbital energies against the momentum values $k_{n}$ determined from the momentum maps, the quasiband structure, or equivalently, the intramolecular band structure can be determined.\textsuperscript{52,60} Several interesting observations can be made when comparing the intramolecular band structures of nAs with those from the DHTA\textsubscript{n} molecules as depicted in Figure 3c. First, all $\pi$ orbitals of the oligoacenes are nicely threaded on the energy bands of a hypothetical, infinitely long polycyclic chain shown as solid and dashed lines. Note that polycyclic actually turns out to be gapless with valence and conduction bands crossing slightly before the Brillouin zone boundary (indicated by a vertical line), but for the sake of comparison, we have shifted the conduction bands of polyacene (dashed lines) such that they match the empty states of the oligoacenes in energy. Second, we observe that all orbital energies of DHTA\textsubscript{n} are, on average, shifted by $\approx 1$ eV to higher binding energies and are slightly more scattered. We also notice a systematic increase in the $k_x$-values from nA to DHTA\textsubscript{n} as indicated by the brown lines connecting black and red circles for $n = 5$. We attribute these effects to the presence of the pyrazine and dihydropyrazine groups that are responsible for the dipole moment of the molecule for which we obtain 3.49, 3.84, and 3.21 debye for $n = 5$, 6, and 7, respectively. As a result of the dipole moment, the electrostatic potential exhibits a step along the long molecular axis, leading to an asymmetric orbital structure and a concomitant deviation from the simple particle-in-a-boxlike band dispersion. The potential step is also responsible for a stronger spatial confinement of the orbital and thereby explains the increased $k_x$-values. A third observation has already been mentioned earlier but can be well-confirmed by plotting the band structure, namely, that the symmetry of the frontier orbitals changes when going from nA to DHTA\textsubscript{9}. While the HOMOs of nA belong to the apex band, $\pi_{20}$, the HOMOs of DHTA\textsubscript{n} for $n = 5, 6, 7$ are rather part of the linking band $\pi_{m,0}$. This results from the presence of two N−H groups that add two more electrons to the $\pi$ system which fill up one more $\pi$ orbital. Similarly, the LUMOs of DHTA have in fact the analogous orbital structure as the LUMO + 1 of the oligoacenes. Last but not the least, the analysis of the $\pi$-band structure of DHTA allows us also to explain the aforementioned peculiar behavior of the IP (the HOMO orbital energy), which remains at an almost constant value of 6.6 eV for $n = 5, 6, 7$ but reduces significantly for the 9- and 11-ring molecules. The reason is that in the case of DHTA\textsubscript{9} and DHTA\textsubscript{11}, the topmost orbital of the apex band, $\pi_{m,1}$ of DHTA\textsubscript{5} is predicted to become the HOMO rather than the highest orbital of the linking band as is the case for $n = 5, 6, 7$.

UV−Vis Absorption Spectra. We have also measured UV−vis absorption spectra of DHTA, DHTA\textsubscript{6}, and DHTA\textsubscript{7} which are depicted as solid lines in Figure 4. All three molecules show two main absorption bands, one in the UV near 300 nm and another in the visible range between 450 and 650 nm. Note that the results for DHTA and DHTA\textsubscript{7} are thus similar to those already observed earlier for the parent system DHTA.\textsuperscript{22} With increasing molecular length, we observe an overall red shift of the absorption features, a phenomenon that is already well-known for oligoacenes and for other aza-acenes.\textsuperscript{21} This can be clearly seen for the peak in the UV, but also the onset of the first excitation shifts to lower
energies, which is in line with a reduction of the HOMO–LUMO gap.

To analyze the experimental observations, we have simulated the vertical excitations energies of DHTAn within the framework of TD-DFT. To account for the solvent, we have considered its dielectric constant, $\varepsilon = 2.18$, in the expression for the exchange correlation energy given by eq 4. Compared to the gas-phase calculations with $\varepsilon = 1$, the dielectric screening in the environment of the solvent leads to a reduction of the single-particle HOMO–LUMO gap from the gas-phase values of 5.60, 5.19, and 5.11 eV for DHTA5, 6, and 7, respectively (see Figure 2), to 3.80, 3.54, and 3.49 eV in the solvent. Focusing on the lowest energy transition, the excitations energies resulting from the TD-DFT calculation turn out to be slightly smaller than those of the HOMO–LUMO gaps, namely, 2.81, 2.61, and 2.62 eV for DHTAs, 6, and 7, respectively. Within our TD-DFT approach and using an OT-RSH functional, this difference between the HOMO–LUMO gap and the optical excitation energy may indeed be interpreted as exciton binding energies with an accuracy comparable to GW-BSE calculations. Thus, we predict exciton binding energies to range between 0.9 and 1.0 eV, which are typical values to be expected for such molecules in a solvent. Note that a reduction of the exciton binding energy is thus nominally expected to be unstable, our computed IPs and EAs reveal the opposite, namely, an increase in IP and a decrease in EA when going from nA to DHTAn for a given number of rings n. This conclusion supports previous works based on the resonance energies, extra cyclic resonance energy, and nucleus independent chemical shift data of 4n $\pi$ electron dihydro-aza-pentacenes which are stabilized by aromativity and conjugations of the dihydroazypentacene moieties. We further predict that all $\pi$ orbitals of DHTAn strongly resemble the one of the parent nA molecules; however, the symmetry of the frontier orbitals changes owing to the addition of two electrons to the $\pi$ system.

Figure 4 shows the lowest 10 excitations of DHTA5 with their corresponding oscillator strengths and a Gaussian broadening of 0.1 eV, which are represented by a black dashed line. Apart from an overall shift of approximately 0.5 eV to higher energies, the simulated spectrum compares quite favorably to the experimental result. With the help of TD-DFT, we can thereby identify the two major absorption bands separated by about 2 eV to arise primarily from the HOMO–LUMO transition and the HOMO – 1/LUMO + 1 transition, respectively. Owing to the symmetry and nodal structure of the involved orbitals (HOMO–LUMO = $\pi_{6s}/\pi_{7s}$ and HOMO – 1/LUMO + 1 = $\pi_{6s}/\pi_{6s}$), both excitations exhibit a transition dipole parallel to the long molecular axis with calculated oscillator strengths of 0.62 and 2.03 whose ratio fits excellently to the experimental spectrum. It is important to note that the optical absorption of DHTA5 therefore distinctly differs from pentacene for which the lowest-lying transition is polarized perpendicular to the molecule.

Finally, also for DHTA6 and DHTA7, the calculations predict the lowest energy transition to be polarized parallel to the long molecular axis. Moreover, also the second major absorption bands of DHTA6 and DHTA7 around 4.34 and 4.26 eV, respectively, mainly arise from the HOMO–LUMO + 2 transition polarized parallel to the long axis. Compared to the experiment, a similar shift of about 0.5 eV for both absorption bands is observed. One reason for this discrepancy could be the fact that the effect of the solvent is taken into account only by its dielectric constant, while for a more accurate description of the spectra a more realistic description of the molecule–solvent interactions may be necessary. Also note that the line structure apparent in the lowest energy absorption band in the experiment is likely due to a vibrational progression which is not taken into account in the theoretical spectra.

## CONCLUSIONS AND OUTLOOK

Building on the already reported synthesis root for DHTA5, in this work, we have succeeded to synthesize and isolate the longer DHTA6 and DHTA7 molecules which we have characterized, both, experimentally and by means of density functional calculations with a nonempirically tuned RSH functional. We have computed the gas-phase electronic structure of linear oligoacene (nA) derivatives in which the benzene rings left and right to the central ring are replaced by rings containing a pyrazine and a dihydropyrazine group, respectively. Despite the fact that such dihydro-tetraaza-acenes (DHTAn, compare Scheme 1) contain 4n $\pi$ electrons and are thus nominally expected to be unstable, our computed IPs and EAs reveal the opposite, namely, an increase in IP and a decrease in EA when going from nA to DHTAn for a given number of rings n. This conclusion supports previous works based on the resonance energies, extra cyclic resonance energy, and nucleus independent chemical shift data of 4n $\pi$ electron dihydro-aza-pentacenes which are stabilized by aromativity and conjugations of the dihydroazypentacene moieties. We further predict that all $\pi$ orbitals of DHTAn strongly resemble the one of the parent nA molecules; however, the symmetry of the frontier orbitals changes owing to the addition of two electrons to the $\pi$ system.

We have also computed photoemission momentum maps for DHTAn which, in future studies, should be tested against experimental observations and could confirm the orbital energies and spatial structure of the frontier orbitals. As a first step toward this direction, we have measured the UV–vis absorption spectra of DHTAs, 6, and 7 in solution and compared them to TD-DFT results. This allows us to identify the origin and polarization of the main optical transitions which are distinctly different from the parent oligoacene series. Moreover, preliminary investigations on the intermolecular packing of DHTAn have emphasized the pronounced role of the molecule’s dipole moment and the importance of hydrogen bonding for these DHTAn molecules. In view of applications in organic electronics, the intramolecular electronic structure together with the expected intermolecular bonding forces...
makes DHTA\textsubscript{n} molecules an interesting class of molecules that certainly deserve further investigations regarding thin-film morphologies and bulk electronic structure.

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\section*{Notes}
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\section*{REFERENCES}

(1) Klauk, H.; Zschieschang, U.; Pflaum, J.; Halik, M. Ultralow-Power Organic Complementary Circuits. Nature 2007, 445, 745–748.

(2) Kitamura, M.; Arakawa, Y. Pentacene-Based Organic Field-Effect Transistors. J. Phys.: Condens. Matter 2008, 20, 184011.

(3) Bredas, J. L.; Calbert, J. P.; da Silva Filho, D. A.; Cornil, J. Organic Semiconductors: A Theoretical Characterization of the Basic Parameters Governing Charge Transport. Proc. Natl. Acad. Sci. U.S.A. 2002, 99, 804–809.

(4) Cheng, Y. C.; Silbey, R. J.; da Silva Filho, D. A.; Calbert, J. P.; Cornil, J. J.; Bredas, J. L. Three-Dimensional Band Structure and Bandlike Mobility in Oligoacene Single Crystals: A Theoretical Investigation. J. Chem. Phys. 2007, 118, 3764.

(5) Hummer, K.; Ambrosch-Draxl, C. Electronic Properties of Oligoacenes from First Principles. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 72, 205205.

(6) Nabok, D.; Puschnig, P.; Ambrosch-Draxl, C.; Werzer, O.; Resel, R.; Smilgies, D.-M. Crystal and Electronic Structures of Pentacene Thin Films from Grazing-Incidence X-Ray Diffraction and First-Principles Calculations. Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 235322.

(7) Sharfizadeh, S.; Biller, A.; Kronik, L.; Neaton, J. B. Quasiparticle and Optical Spectroscopy of the Organic Semiconductors Pentacene and PTCDI from First Principles. Phys. Rev. B: Condens. Matter Mater. Phys. 2012, 85, 125307.

(8) Tiago, M. L.; Northrup, J. E.; Louie, S. G. Ab initio Calculations of the Electronic and Optical Properties of Solid Pentacene. Phys. Rev. B: Condens. Matter Mater. Phys. 2003, 67, 115212.

(9) Hummer, K.; Ambrosch-Draxl, C. Oligoacene Exciton Binding Energies: Their Dependence on Molecular Size. Phys. Rev. B: Condens. Matter Mater. Phys. 2005, 71, No. 081202(R).

(10) Ambrosch-Draxl, C.; Nabok, D.; Puschnig, P.; Meisenbichler, C. The Role of Polymorphism in Organic Thin Films: Oligoacenes Investigated from First Principles. New J. Phys. 2009, 11, 125010.

(11) Rangel, T.; Berland, K.; Sharfizadeh, S.; Brown-Alvater, F.; Lee, K.; Hylgaard, P.; Kronik, L.; Neaton, J. B. Structural and Excited-State Properties of Oligoacene Crystals from First Principles. Phys. Rev. B 2016, 93, 115206.
(35) Kronik, L.; Stein, T.; Refaely-Abramson, S.; Baer, R. Excitation Gaps of Finite-Sized Systems from Optimally Tuned Range-Separated Hybrid Functionals. *J. Chem. Theory Comput.* 2012, 8, 1515–1531.

(36) Lüftner, D.; Refaely-Abramson, S.; Pachler, M.; Resel, R.; Ramsey, M. G.; Kronik, L.; Puschning, P. Experimental and Theoretical Electronic Structure of Quinacridone. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2014, 90, 075204.

(37) Seidl, A.; Görling, A.; Vogl, P.; Majewski, J. A.; Levy, M. Generalized Kohn-Sham Schemes and the Band-Gap Problem. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1996, 53, 3764–3774.

(38) Yanai, T.; Tew, D. P.; Handly, N. C. A New Hybrid Exchange-Correlation Functional Using the Coulomb-Attenuating Method (CAM-B3LYP). *Chem. Phys. Lett.* 2004, 393, 51–57.

(39) Srebro, M.; Autschbach, J. Does a Molecule-Specific Density Functional Give an Accurate Electron Density? The Challenging Case of the CuCl Electric Field Gradient. *J. Phys. Chem. Lett.* 2012, 3, 576–581.

(40) Srebro, M.; Autschbach, J. Tuned Range-Separated Time-Dependent Density Functional Theory Applied to Optical Rotation. *J. Chem. Theory Comput.* 2012, 8, 245–256.

(41) Leininger, T.; Stoll, H.; Werner, H.-J.; Savin, A. Combining Long-Range Configuration Interaction with Short-Range Density Functionals. *Chem. Phys. Lett.* 1997, 275, 151–160.

(42) Stein, T.; Eisenberg, H.; Kronik, L.; Baer, R. Fundamental Gaps in Finite Systems from Eigenvalues of a Generalized Kohn-Sham Method. *Phys. Rev. Lett.* 2010, 105, 266802.

(43) Körzdörfer, T.; Sears, J. S.; Sutton, C.; Brédas, J.-L. Long-Range Corrected Hybrid Functionals for π-Conjugated Systems: Dependence of the Range-Separation Parameter on Conjugation Length. *J. Chem. Phys.* 2011, 135, 204107.

(44) Tamblyn, I.; Refaely-Abramson, S.; Neaton, J. B.; Kronik, L. Simultaneous Determination of Structures, Vibrations, and Frontier Orbital Energies from a Self-Consistent Range-Separated Hybrid Functional. *J. Phys. Chem. Lett.* 2014, 5, 2734–2741.

(45) Perdew, J. P.; Parr, R. G.; Levy, M.; Balduz, J. L. Density-Functional for Fractional Particle Number: Derivative Discontinuities of the Energy. *Phys. Rev. Lett.* 1982, 49, 1691.

(46) Levy, M.; Perdew, J. P.; Sahni, V. Exact Differential Equation for the Density and Ionization Energy of a Many-Particle System. *Phys. Rev. A* 1984, 30, 2745–2748.

(47) Almbladh, C.-O.; von Barth, U. Exact Results for the Charge and Spin Densities, Exchange-Correlation Potentials, and Density-Functional Eigenvalues. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1985, 31, 3231–3244.

(48) Perdew, J. P.; Levy, M. Comment on “Significance of the Highest Occupied Kohn-Sham Eigenvalue”. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1997, 56, 16021–16028.

(49) Rohrdanz, M. A.; Herbert, J. M. Simultaneous Benchmarking of Ground- and Excited-State Properties with Long-Range-Corrected Density Functional Theory. *J. Chem. Phys.* 2008, 129, 034107.

(50) Casida, M. Time-Dependent Density-Functional Response Theory for Molecules. In *Recent Advances in Density Functional Methods*; Chong, D., Ed.; World Scientific: Singapore, 1995; p 155

(51) Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apri, E.; Windus, T. L.; et al. NWChem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. *Comput. Phys. Commun.* 2010, 181, 1477–1489.

(52) Berkebile, S.; Puschning, P.; Koller, G.; Oehzelt, M.; Netzer, F. P.; Ambrosch-Draxl, C.; Ramsey, M. G. Electronic Band Structure of Pentacene: An Experimental and Theoretical Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2008, 77, 115312.

(53) Lüftner, D.; Ules, T.; Reinisch, E. M.; Koller, G.; Soubatch, S.; Tautz, F. S.; Ramsey, M. G.; Puschning, P. Imaging the Wave Functions of Adsorbed Molecules. *Proc. Natl. Acad. Sci. U.S.A.* 2014, 111, 605–610.

(54) Clark, P. A.; Brogli, F.; Heilbrunner, E. The π-Orbital Energies of the Aces. *Helv. Chim. Acta* 1972, 55, 1415–1428.

(55) Croker, L.; Wang, T.; Kedarle, P. Electron Affinities of Some Polycyclic Aromatic Hydrocarbons, Obtained from Electron-Transfer Equilibria. *J. Am. Chem. Soc.* 1993, 115, 7818–7822.

(56) Puschning, P.; Berkebile, S.; Fleming, A. J.; Koller, G.; Emtsev, K.; Seyller, T.; Riley, J. D.; Ambrosch-Draxl, C.; Netzer, F. P.; Ramsey, M. G. Reconstruction of Molecular Orbital Densities from Photoemission Data. *Science* 2009, 326, 702–706.

(57) Ules, T.; Lüftner, D.; Reinisch, E. M.; Koller, G.; Puschning, P.; Ramsey, M. G. Orbital Tomography of Hybridized and Dispersing Molecular Overlayers. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2014, 90, 155430.

(58) Hollerer, M.; Lüftner, D.; Hurda, P.; Ules, T.; Soubach, S.; Tautz, F. S.; Koller, G.; Puschning, P.; Sterrer, R.; Ramsey, M. G. Charge Transfer and Orbital Level Alignment at Inorganic/Organic Interfaces: The Role of Dielectric Interlayers. *ACS Nano* 2017, 11, 6525–6530.

(59) Puschning, P.; Ramsey, M. Reference Module in Chemistry, Molecular Sciences and Chemical Engineering; Elsevier, 2017.

(60) Koller, G.; Berkebile, S.; Oehzelt, M.; Puschning, P.; Ambrosch-Draxl, C.; Netzer, F. P.; Ramsey, M. G. Intr- and Intermolecular Band Dispersion in an Organic Crystal. *Science* 2007, 317, 351–355.

(61) Refaely-Abramson, S.; Jain, M.; Sharifzadeh, S.; Neaton, J. B.; Kronik, L. Solid-State Optical Absorption from Optimally Tuned Time-Dependent Range-Separated Hybrid Density Functional Theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2015, 92, 081204.

(62) Puschning, P.; Ambrosch-Draxl, C. Suppression of Electron-Hole Correlations in 3D Polymer Materials. *Phys. Rev. Lett.* 2002, 89, 056405.

(63) Cocchi, C.; Draxl, C. Optical Spectra from Molecules to Crystals: Insight from Many-Body Perturbation Theory. *Phys. Rev. B: Condens. Matter Mater. Phys.* 2015, 92, 205126.