

Stacking Interactions

Competition Between π - π and C-H/ π Interactions: A Comparison of the Structural and Electronic Properties of Alkoxy-Substituted 1,8-Bis((propyloxyphenyl)ethynyl)naphthalenes

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In memory of Professor Herbert O. House

Abstract: The structural and electronic consequences of π - π and C–H/ π interactions in two alkoxy-substituted 1,8-bis-((propyloxyphenyl)ethynyl)naphthalenes are explored by using X-ray crystallography and electronic structure computations. The crystal structure of analogue **4**, bearing an alkoxy side chain in the 4-position of each of the phenyl rings, adopts a π -stacked geometry, whereas analogue **8**, bearing alkoxy groups at both the 2- and the 5-positions of each ring, has a geometry in which the rings are splayed away from a π -stacked arrangement. Symmetry-adapted perturbation theory analysis was performed on the two analogues to evaluate the interactions between the phenylethynyl arms in each molecule in terms of electrostatic, steric, polarization, and London dispersion components. The computations support the expectation that the π -stacked geometry of the alkoxyphenyl units in **4** is simply a consequence of maximizing π - π interactions. However, the splayed geometry of **8** results from a more subtle competition between different noncovalent interactions: this geometry provides a favorable anti-alignment of C–O bond dipoles, and two C–H/ π interactions in which hydrogen atoms of the alkyl side chains interact favorably with the π electrons of the other phenyl ring. These favorable interactions overcome competing π - π interactions to give rise to a geometry in which the phenylethynyl substituents are in an offset, unstacked arrangement.

Introduction

Interactions between π -conjugated units (π – π interactions) are ubiquitous in chemistry. They contribute to a variety of phenomena including the structure of biomolecules (proteins,^[1] DNA/RNA^[2]), drug binding,^[3] and catalytic function.^[4] π -Interactions are also important to charge transport in semiconducting π -conjugated materials in the development of devices such as organic thin-film transistors,^[5] photovoltaic solar cells,^[6] and

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light-emitting diodes.^[7] The charge transport properties of conjugated oligomers and polymers depend strongly on their molecular packing, with contributions from both the orientation and distance between the π -systems of neighboring molecules.^[8] Side chains also have a strong influence on the packing of conjugated units. The latter rises from the segregation of semi-rigid conjugated segments and flexible side chains, and from side chain crystallization of regularly-placed linear alkyl substituents.^[9]

Gaining an understanding of the propensity for π -systems to stack with one another and the influence of intermolecular interactions on the properties of such assemblies is crucial to the further development of diverse fields. A good understanding of π - π interactions includes facets such as strength, geometry dependence, and tunability through changes in the nature of substituents or aromatic units. Such questions have been addressed both experimentally and theoretically (for reviews see refs.^[10]).

Frustratingly, theoretical and experimental results have been at odds regarding substituent effects in π -stacked systems. Numerous experiments are consistent with the Hunter–Sanders rules,^[11] which posit that substituent effects in π -stacking interactions are governed by electrostatic factors: electron-withdrawing substituents reduce the extent of unfavorable Coulombic interactions between the electron-rich π -clouds, thus strengthening the interaction, whereas electron-donating sub-

Chem. Eur. J. 2015, 21, 19168-19175

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stituents have the opposite effect. By contrast, high-level wavefunction-based theoretical studies show definitively that in the gas phase, both electron-donating and electron-with-drawing substituents lead to stronger π - π interactions in cofacial geometries.^[12] To date, only limited experimental work seems to support the latter conclusion.^[13] Other theoretical work by Wheeler and co-workers indicates that substituents do not actually tune the π -electron density, but instead exert their influence by direct, through-space interactions with the other π -system.^[15] The recently developed functional-group-based partitioning of symmetry-adapted perturbation theory^[16] (F-SAPT) supports the Wheeler–Houk view for substituted cofacial benzene dimers.^[17]

To better understand how substituents affect π -stacking, we report the synthesis, structural characterization, and theoretical analysis of two alkoxy-substituted 1,8-bis(phenylethynyl)naphthalenes, 4 and 8. The 1,8-naphthlene core holds two conjugated phenylethynyl units in close proximity such that these molecules can be considered as models for two interacting chains of poly(phenylene ethynylene).^[18] The availability of such molecular models for interacting repeat units of conjugated polymers affords the opportunity to gain detailed structural information from X-ray crystallography and to perform computations to gain further insights into the factors that influence π -stacking. Several prior reports have described π -stacking interactions of arenes that are attached to a 1,8-naphthalenediyl scaffold. House reported the X-ray crystal structures and bond rotation energy barriers of various substituted 1,8-diphenylnapthalenes and noted significant deformation from a cofacial geometry.^[19] Cozzi and Siegel used 2-D NMR spectroscopic techniques to determine the barrier to rotation of the phenylene units,^[20] which they found to correlate with Hammett σ_{para} values, supporting the Hunter–Sanders rules if one assumes that the barrier is increased or decreased according to the substituent effect on the π -stacking interaction. This interpretation of the data is, however, somewhat problematic in that substituents will affect both the potential energy minimum as well as the transition state for rotation, so that variations in measured barriers (ΔG^{\pm}) do not necessarily correspond directly to variations in cofacial π - π interactions.

Results and Discussion

Synthesis and structural characterization of 1,8-bis(phenylethynyl)naphthalenes 4 and 8

For this study, we explored two alkoxy-substituted 1,8-bis((propyloxyphenyl)ethynyl)naphthalenes: an analogue bearing alkoxy groups in the 4-position of the phenyl rings (**4**), and a second that bears alkoxy groups at both the 2- and the 5-positions of each ring (**8**). The synthesis of the bis((4-propyloxyphenyl)ethynyl) derivative **4** is shown in Scheme 1 A. Coupling of 4-iodo-1-propyloxybenzene (**1**) with propargyl alcohol under Sonogashira conditions^[21] gave alcohol **2**, which was converted into terminal acetylene **3** under oxidizing conditions. Installation of ethynyl groups in this fashion proved more effective than making use of trimethylsilylacetylene followed by desilylation because separation of the monopropargylated synthetic intermediate from byproducts was simplified because of the



Scheme 1. Synthesis of substituted 1,8-bis(phenylethynyl)naphthalenes 4 and 8. a) 1,8-bis((4-propyloxyphenyl)ethynyl)naphthalene (4). b) 1,8-Bis(4-propyloxyphenyl)ethynylnaphthalene (8).

Chem. Eur. J. 2015, 21, 19168-19175

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19169

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polarity introduced in this step by incorporation of an alcohol. Coupling of **3** and 1,8-diiodonaphthalene under Sonogashira conditions afforded **4**.^[22]

The synthesis of the bis((2,5-dipropyloxyphenyl)ethynyl) derivative 8 followed a similar route, as shown in Scheme 1B. Treatment of 1,4-dipropoxybenzene with one equivalent of iodine resulted in monoiodo arene 5, although formation of some diiodinated by-product could not be avoided. In optimizing the overall process, treatment of the crude product of this reaction with an excess of propargyl alcohol under Sonogashira coupling conditions provided the monopropargylated benzene, 6, which was easily separated from the bis(propargyl) compound by column chromatography. The alcohol was then oxidized to acetylene 7 to afford 2-ethynyl-1,4-dipropyloxybenzene and subsequently coupled to 1,8-diiodonaphthalene under the same Sonogashira coupling conditions to afford 8. The structures of 1,8-bis(phenylethynyl)naphthalenes 4 and 8 were verified by ¹H NMR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information for spectra). Signals corresponding to the naphthalene hydrogen atoms show a small but distinct dependence on the substitution of the phenylethynyl unit. Whereas signals for H2 and H4 of 4 appear as doublets $({}^{2}J(2,3) = {}^{2}J(3,4) = 8$ Hz), those of **8** appear as distinctive doublet of doublets $({}^{2}J(2,3) = {}^{2}J(3,4) = 7$ Hz; ${}^{3}J =$ 1 Hz).

Single crystals of 4 and 8 that were suitable for X-ray crystallography were prepared by slow evaporation of solvent from a 1:10 solution of ethyl acetate in hexanes over 12 h at room temperature. The crystal structure of the (4-propyloxyphenyl) analogue 4 is shown along three axes in Figure 1 (left). As expected, the naphthalene unit is predominantly planar. However, there is some in-plane distortion of the substituents at the 1- and 8-positions, with an angle defined by carbon atoms C8-C1-C13 of 97° (and \angle C1-C8-C13′ = 97°). Crowding of the phenylethynyl substituents is further accommodated by a bending around the ethynyl carbon atoms (&C1-C11-C12 + &C11-C12- $C13 = 349^{\circ}$; $\& C8-C11'-C12' + \& C11'-C12'-C13' = 349^{\circ}$). There is very little out-of-plane distortion, with the ethynyl substituents lying in the plane of the naphthalene (Figure 1, left middle). The phenyl rings of the phenylethynyl arms of 4 are arranged in a tilted stack at an angle 115° relative to the naphthalene scaffold (Figure 1, bottom left), which is similar to the tilting of the phenyl rings of 1,8-diphenylnaphthalene (i.e., an analogue of the skeleton of **4** without the ethynylene linkages).^[19b] Such tilted stacks are common to the crystal structure of fused and linear conjugated arenes,^[23] in organic semiconductors,^[24] and columnar discotic phases.^[25] The phenyl rings of **4** are almost parallel, with an intercentroid distance of 3.7 Å. Relative to the normal to the planes represented by the phenyl rings, there is a stacked vertical separation, $R_{\rm V}$ of 3.1 Å and a horizontal displacement $R_{\rm H}$ of 1.8 Å. Accordingly, this arrangement of arenes mimics that commonly found in crystalline regions of conjugated polymers, in discotic liquid crystals, and in stacks of DNA base pairs. It is similar to, but somewhat closer than, the calculated geometry of the energetic minimum of the parallel-displaced configuration of the benzene dimer ($R_v = 3.5$ Å, $R_H =$ 1.7 Å).^[26]

Numbering scheme for discussion of crystal structures





bis(2,5-dipropyloxyphenyl) analogue 8



Figure 1. Molecular structures and key parameters determined by X-ray crystallography. Left: 1,8-bis((4-propyloxyphenyl)ethynyl)naphthalene (4). Right: 1,8-Bis((2,5-dipropyloxyphenyl)ethynyl)naphthalene (8). Note that angles reflect distortions in three dimensions and propyl groups are omitted for clarity

This stacked architecture is in sharp contrast to the geometry of the bis(2,5-dipropyloxyphenyl) analogue **8** (Figure 1, right). In this case, in addition to a greater in-plane distortion, there is a significant amount of out-of-plane deformation. The

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in-plane distortion of the substituents at the 1- and 8-positions as characterized by the angle C8-C1-C13 is 103° (and \gtrless C1-C8- $C13' = 102^{\circ}$), compared with 97° for the respective positions of 4 (Figure 1, top right). In addition, the ethynylene linkages deviate from linearity for 8 (\angle C1-C11-C12+ \angle C11-C12-C13= 347°; ≩C8-C11′-C12′ + ≩C11′-C12′-C13′ = 347°). There is significant out-of-plane bending that is characterized by a torsional angle τ (C16-C1-C8-C16') = 26° (Figure 1, middle right). The combination of in-plane and out-of-plane distortions results in a structure in which the phenyl rings are not arranged in a stacked fashion. In this case, and in contrast to the situation for 4, the phenyl rings are almost parallel with the naphthalene scaffold, tilted by ca. 15° and 8° (Figure 1, bottom right), compared with 115° in 4, and they are significantly offset from one another with a vertical separation of $R_{\rm V}$ = 3.1 Å and horizontal displacement of $R_{\rm H} = 4.7$ Å. Although there is precedence for dramatic in-plane and out-of-plane bending of arene units,^[27] including 1,8-disubstituted anthracenes,[28] we were surprised by the dissimilarity of the geometries of 4 and 8 that arise from differences in the substitution pattern of the phenylethynyl arms. Alkoxy and alkyl side chains are common features on conjugated polymers and oligomers, including poly(phenylene acetylenes), and discotic liquid crystals. These side chains are accommodated by, and support the formation of, the stacked arrangement of the π -systems.

The minor distortions from a cofacial geometry in 4, and the major deviations away from a π -stacking geometry in 8 might be ascribed to a combination of steric and Coulombic repulsions between electron-rich phenyl rings, with the dialkoxysubstituted phenyl rings in 8 being more electron-rich and thus, perhaps, resulting in greater distortions. Such an interpretation would be consistent with the analysis of Cozzi and Siegel^[20] for the rotation barriers in their biaryInaphthalenes, indicating that π - π interactions are stronger with electronwithdrawing substituents and weaker for electron-donating substituents (one of the Hunter-Sanders rules). On the other hand, recent high-accuracy quantum chemical computations in the gas phase indicate that all substituents, regardless of electron-donating or electron-withdrawing character, stabilize $\pi - \pi$ interactions in cofacial phenyl rings.^[12] Based on the prior experimental results reported by Carey et al. for 3,5-substituted arenes,^[13b,c] it is surprising that **8** does not adopt a geometry that is even more aligned for π -stacking than that of 4; apparently, the proximity of the arenes causes C--H/ π interactions to draw the arenes out of plane and dominate the conformation of the molecule. Hence, we performed electronic structure computations to understand this difference.

Computational analysis

The interactions between the substituted phenyl rings of **4** and **8** were examined by using density-fitted functional group symmetry-adapted perturbation theory^[16,17,29] truncated at zeroth-order intramonomer correlation^[30] (F-SAPT0) combined with the jun-cc-pVDZ basis set,^[31] which is Dunning's aug-cc-pVDZ set^[32] without diffuse functions on hydrogen and without diffuse d functions on heavy atoms (this basis set has pre-

viously been used by our group under the name aug-ccpVDZ'). This level of theory not only gives reasonably accurate energies^[33] for noncovalent interactions, but also decomposes the interaction into the physically meaningful components of electrostatics, exchange-repulsion (sterics), induction (polarization), and London dispersion forces to better understand the physical nature of the interaction. Functional group SAPT can further break down these interaction energy components into contributions from each molecular sub-fragment (a group of atoms chosen by the user).

In the course of analyzing nonbonding contacts in **4** and **8** and their potential influence on the preferred geometries in these compounds, it is important to bear in mind that crystal-packing forces may also exhibit a significant influence. However, gas-phase optimizations of **4** and **8** at the B3LYP-D/aug-cc-pVDZ level of theory result in conformations similar to those in the crystal structures (see Figure S25 and S26 of the Supporting Information).^[34] Intramolecular interactions are enhanced slightly (see Figure S29), but our conclusions remain the same using these optimized geometries. The unusually strained geometry optimization using standard quantum program packages. Enhancements to the optimizer in the Psi4 program^[35] allowed the optimizations to be completed.

In the computations, the naphthalene and ethynyl linkers were removed from each compound for simplicity of analysis and to provide the distinct molecular fragments necessary for SAPT analysis. Severed covalent bonds were capped with hydrogen atoms subject to constrained optimizations (keeping all other nuclei fixed) at the B3LYP-D/aug-cc-pVDZ level of theory. F-SAPT fragments were chosen to be the propyl groups (one in each monomer for **4**, and two in each monomer for **8**) and the aryl ring plus attached oxygen atoms, as indicated in Figure 2.

All SAPT computations were performed within Psi4. Constrained optimizations to place capping hydrogen atoms were performed using the Q-Chem package.^[36] Figure S27 and S28 contain the F-SAPT0/jun-cc-pVDZ energy components for the interaction between the pairs of mono- or di-propyloxybenzenes (models of the arms in 4 and 8, respectively). The overall interaction energies between each pair of model fragments are provided in the color-coded diagrams in Figure 2. The dipropyloxybenzenes of the model for 8 interact nearly twice as strongly as the mono-propyloxybenzenes of 4 (interaction energies of -6.9 versus -3.6 kcal mol⁻¹; more negative values indicate stronger intermolecular attractions). The phenyl rings of 4 are at a vertical separation of $R_v = 3.1$ Å and a horizontal displacement of $R_{\rm H} = 1.8$ Å. The interaction of the oxyphenyl portion of the molecule alone accounts for 70% ($-2.5 \text{ kcal mol}^{-1}$) of the model propyloxybenzene-propyloxybenzene interaction for 4. This interaction is dominated by dispersion, but contains significant attractive electrostatics (see Figure S27). The interaction of each oxyphenyl unit with each propyl fragment $(-0.5\;kcal\,mol^{-1})$ and the interaction of the propyl fragments $(-0.1 \text{ kcal mol}^{-1})$ both arise primarily from dispersion forces. The offset-stacked nature of the mono-propyloxybenzene units of 4 keeps the electronegative oxygen atoms from being

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Figure 2. Interaction energies (kcal mol⁻¹) and geometries: a) propyloxybenzenes as models of interactions in **4**; b) *para*-dipropyloxybenzenes as models of interactions in **8**; c) propyloxybenzenes as models for units of **4** in the phenyl ring geometry of **8** (model system **85**); and d) *para*-dipropyloxybenzenes as models for units of **8** in the phenyl ring geometry of **8** (model system **45**) are presented on the left of each section (light brown to brown). F-SAPTO/jun-cc-pVDZ^[16] interaction energies between propyl and/or aryl molecular fragments are presented at the top of each section by color. The diamonds indicate the phenyl carbon atoms that are connected through the ethynyl linkages to the 1,8-naphthalene scaffold. Negative values for interaction energies indicate an attractive interaction.

stacked directly on top of each other, which would otherwise make an unfavorable contribution to the electrostatic term. The phenyl rings of **8** are angled 35° from being parallel and are displaced more horizontally (R_V =3.1 Å, R_H =4.7 Å) than in **4**. For cofacial benzene dimers, all substituents are known to increase the strength of π - π interactions in gas-phase computations, regardless of electron-donating or electron-withdrawing character.^[12a] Thus, it may be surprising that the disubstituted phenylenes in **8** adopt a less cofacial geometry than does **4**. The interaction of the two model oxygen-substituted aryl fragments in **8** is -5.2 kcal mol⁻¹, which is due to electrostatics and dispersion. The favorable anti-alignment of two polar O–C bonds of **8** contributes significantly to this favorable electrostatic stabilization (see Figure 2 b for geometry). In addition, the crystal structure of **8** contains two close C–H/ π contacts, in which a hydrogen atom of a propyl chain of one phenyl ring is in a position to interact favorably with the π cloud of the second phenyl ring (with distances of 3.1 and



Figure 3. Side view of **8** illustrating one of the two C–H/ π interactions.

3.2 Å between the hydrogen atoms and the centers of the aromatic rings; see Figure 3 for an illustration of one of these C– H/ π contacts). Computations indicate that these interactions are dispersion dominated, with each C–H/ π interaction contributing –0.6 kcal mol⁻¹ to the interaction energy. A large spatial separation of the phenyl rings is necessary to achieve this arrangement of mutual C–H/ π interactions and C–O bond antialignment, thereby explaining the deviation of **8** from any traditional π -stacking geometry.

To further investigate the surprising differences between the expected and observed geometry of the π systems in 8, computational experiments were performed on hypothetical "switched" model systems in which the propyloxy substituents are exchanged between compounds 4 and 8. Compound 4 had its single propyloxy substituent on each phenyl switched for two propyloxy substituents to yield model 4S. This hypothetical structure illustrates what the dipropyloxy compound 8 would look like if it adopted an offset-stacked arrangement of the phenyl rings (like that in 4) instead of the splayed arrangement it actually has [see Figure 2(c), (d)]. Comparing the F-SAPT energetics for 8 versus 4S provides further insight into why the dipropyloxy compound 8 adopts its "native" splayed structure instead of an offset-stacked one like that of compound 4. For this comparison we compute only the interactions between the alkoxy-substituted phenyl arms (replacing the linkage to the backbone with a capping hydrogen atom), as in the previous discussion of the F-SAPT results for 4 and 8. The substituent geometry was refined by a constrained optimization, keeping the coordinates of the phenyl rings fixed.

The attraction between the two dioxyphenyl moieties in the stacked phenyl ring geometry of **4S** (-4.0 kcal mol⁻¹) is much greater than that between the two oxyphenyl components in **4** (-2.5 kcal mol⁻¹). This is consistent with previous observations that increasing substitution of phenyl rings leads to increased attraction for π - π stacking.^[12] However, a steric clash between two of the propyl groups in the stacked dipropyloxybenzene model **4S** (+2.7 kcal mol⁻¹, **4S**·PrB-**4**S·PrA' in Figure 2 (d)) more than cancels out this enhancement of the π - π

interaction. Moreover, the π -stacked geometry in **4S** also removes the two favorable C–H/ π interactions and C–O dipole anti-alignment that were found in **8**. Overall, then, total interactions between two dipropyloxybenzenes are significantly more favorable (-6.9 kcalmol⁻¹) in the experimentally observed splayed geometry of **8** than they are in the π -stacked geometry **4S** (-3.7 kcalmol⁻¹), even though the π - π interaction strength is increased by additional substituents in **4S** relative to **4**.

We have performed a similar comparison between the mono-propyloxy substituted system **4** in its native, offsetstacked geometry and a hypothetical geometry in which we take the geometry of **8** and switch its dipropyloxy substitution pattern on each phenyl for a single mono-propyloxy substituent (model **8 S**). The experimentally observed π -stacked geometry **4** is significantly more favorable for interactions between two mono-propyloxybenzenes ($-3.6 \text{ kcal mol}^{-1}$) than is the more open geometry of **8 S** ($-1.6 \text{ kcal mol}^{-1}$). This is simply a consequence of the stacked geometry being more favorable for π - π interactions ($-2.5 \text{ vs.} -1.4 \text{ kcal mol}^{-1}$ in **4** vs. **8 S**) and the propyl groups of **8 S** being too far apart to interact.

In summary, computations based on models for subunits of 4 and 8 indicate that the propyloxyphenyl subunits of 4 interact with $-3.6 \text{ kcal mol}^{-1}$ of energy resulting from an optimal parallel-displaced π -stacking geometry. The dipropyloxyphenyl subunits of **8** interact more strongly $(-6.9 \text{ kcal mol}^{-1} \text{ overall})$ in a conformation that has a larger separation of the π systems, but also two favorable C–H/ π interactions of -0.6 kcal mol⁻¹ each and a favorable C-O dipole anti-alignment in the substituents. Thus, each system adopts a geometry that maximizes the overall sum of the available noncovalent interactions. Performing the computational experiment of switching the substituents between models 4 and 8 at fixed phenyl ring geometry results in interactions that are less than ideal, including steric clashes for 4S, and weakly interacting propyloxybenzenes for 8S without the stabilization of the C–H/ $\!\pi$ interactions.

Conclusion

We have presented one of the first detailed case studies of a competition between C–H/ π and π - π interactions, and we have explored how this competition influences molecular structure in the two alkoxy-substituted 1,8-bis((propyloxyphenyl)ethynyl) naphthalenes examined. Additional studies on related systems (e.g., with different alkoxy substituents, or with electron-withdrawing substituents) would certainly be warranted; nevertheless, the present comparison yields several interesting conclusions. The rather different geometries adopted by **4** and **8** cannot be understood by considering π - π interactions alone (indeed, with respect to π - π interactions only, the 2,5-dipropyloxy phenyl groups in 8 actually prefer a more stacked geometry like that in 4). Instead, other interactions (such as the favorable anti-alignment of C-O bond dipoles and the favorable C–H/ π interactions that can result from the less π stacked geometry of 8) must also be taken into account. By using the newly-developed fragment-based symmetry-adapted



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perturbation theory (F-SAPT), we show that electrostatic effects alone are also insufficient to explain the geometric preferences in these systems. The delicate interplay between different non-covalent interactions must therefore be kept in mind in future efforts to understand and design the structures of π -conjugated materials.

Experimental Section

General procedures

All reactions were conducted in freshly-distilled solvents in ovendried and argon-charged glassware. All reagents were used as received from commercial suppliers without additional purification. Analytical thin-layer chromatography (TLC) was performed on precoated aluminum-backed plates purchased from Sorbent Technologies (silica gel 60 F254; 0.25 mm thickness). Flash column chromatography was performed on silica gel 60 (230–400 mesh ASTM) from Sorbent Technologies. ¹H and ¹³C NMR spectra were recorded with a Varian Gemini spectrometer (300 MHz for ¹H and 75 MHz for ¹³C) in deuterated chloroform (CDCl₃) and referenced to peaks for chloroform (CHCl₃) at δ =7.26 ppm (¹H) and δ =77.0 ppm (¹³C). Chemical shifts are reported in parts per million (ppm). Abbreviations for signal multiplets are as follows: s, singlet; d, doublet; t, triplet; m, multiplet (br=broad).

IR spectra of neat films were collected with a Nicolet 4700 FTIR fitted with an ATR attachment from SmartOrbit Thermoelectronic Corp. Mass spectra were recorded with a MALDI Micromass TOF Spec2E instrument or by using El with a Waters 70SE instrument. Elemental analyses were obtained from Atlantic Microlabs (Norcross, Georgia). X-ray crystal structures were collected with a Bruker Apex-II CCD by Kenneth Hardcastle at the Emory University X-ray facility.

1,8-Bis((4-propyloxyphenyl)ethynyl)naphthalene (4)

A solution of 1,8-diiodonaphthalene (0.260 g, 664 μ mol), 3 (0.548 g, 3.42 mmol), [Pd(Ph₃P)₂Cl₂] (48 mg, 68 µmol), and Cul (130 mg, 68.3 $\mu mol)$ in a 1:2 solution of piperidine in THF (13 mL) was heated to 70 $^\circ\text{C}$ under Ar for 12 h. The mixture was extracted with Et₂O (30 mL) and washed with saturated aqueous NH₄Cl (100 mL) and H₂O (100 mL). The solvent was removed under reduced pressure and the residue was subjected to column chromatography (ethyl acetate/hexanes, 1:10) to afford 4 (140 mg, 47%) as an offwhite solid. M.p. 116–119 °C; ¹H NMR (CDCl₃): $\delta = 1.04$ (t, J = 7 Hz, 6H; CH₃), 1.80 (sextet, ³J=7 Hz, 4H; CH₂), 3.86 (t, J=7 Hz, 4H; OCH₂), 6.67 (d, J=9 Hz, 4H; Ar-H), 7.30 (d, J=9 Hz, 4H; Ar-H), 7.44 (dd, J=8 Hz, 2H; naphthyl H3 and H6), 7.80 (d, J=8 Hz, 2H; naphthyl-H), 7.85 ppm (d, J=8 Hz, 2 H; naphthyl-H); $^{\rm 13}{\rm CNMR}$ (CDCl₃): $\delta =$ 10.5 (CH₃), 22.5 (CH₂), 69.4 (OCH₂), 88.4 (=C), 96.8 (=C), 114.1, 115.8, 121.2, 125.5, 129.2, 131.4, 133.0, 134.1, 134.5, 158.8 ppm; IR (AT-IR, neat): $\tilde{\nu} = 3050$, 2963, 2933, 2870, 2200, 1605, 1562, 1509, 1246, 825 cm⁻¹; MS (EI): m/z (%): 444.1 (100) [M^+], 359.1 (10) [$M^+-2\times$ C₃H₇], 331.1 (10); HRMS: *m/z* calcd for C₃₂H₂₈O₂: 444.20893; found: 444.20716 ($\Delta =$ 4.0 ppm).

1,8-Bis((2,5-dipropyloxyphenyl)ethynyl)naphthalene (8)

A solution of 1,8-diiodonaphthalene (500 mg, 1.32 mmol), **7** (717 mg, 3.30 mmol), [Pd(Ph₃P)₂Cl₂] (23 mg, 33 µmol), and Cul (13 mg, 66 µmol) in a 1:2 solution of piperidine in THF (30 mL) under Ar was stirred at 70 °C for 12 h. Et₂O (100 mL) was added and the mixture was washed with saturated aqueous NH₄Cl

(100 mL), and H_2O (100 mL). The solvent was removed under reduced pressure and the residue subjected to column chromatography (ethyl acetate/hexanes, 1:20) followed by recrystallization from MeOH to give 8 (482 mg, 65%) as a light-beige solid. M.p. = 79-80°C; ¹H NMR (CDCl₃): $\delta = 0.91$ (t, J = 7 Hz, 6H; CH₃), 1.08 (t, J = 1.007 Hz, 6H; CH₃), 1.61 (sextet, ${}^{3}J=7$ Hz, 2H; CH₂), 1.86 (sextet, ${}^{3}J=7$ 7 Hz, 2H; CH₂), 3.37 (t, J=7 Hz, 4H; OCH₂) 3.89 (t, J=7 Hz, 4H; OCH₂), 6.72–6.75 (m, 4H; Ar-H), 6.78–6.82 (m, 2H; Ar-H), 7.47 (t, J= 7 Hz, 2H; naphthyl H3 and H6), 7.81 (d, J=7 Hz, 2H; naphthyl-H), 7.88 ppm (d, J = 7 Hz, 2H; naphthyl-H); ¹³C NMR (CDCl₃): $\delta = 10.7$ (CH₃), 10.9 (CH₃), 22.8 (CH₂), 23.0 (CH₂), 69.7(OCH₂), 71.3 (OCH₂), 93.9 (C=C), 94.1 (C=C), 113.8, 114.3, 117.1, 117.8, 121.7, 125.8, 129.5, 131.4, 134.3, 135.0, 152.8 (CO-Ar), 154.3 ppm (CO-Ar); IR (AT-IR, neat): $\tilde{\nu} = 2957$, 2930, 2870, 2359, 2196, 1595, 1495, 1216, 978 cm⁻¹; MS (EI): *m/z* (%): 560.3 (100) [*M*⁺], 517.3 (60) [*M*⁺-C₃H₇]; HRMS: m/z calcd for C₃₈H₄₀O₄: 560.29029; found: 560.29266 ($\Delta =$ 4.2 ppm); elemental analysis calcd (%) for C₃₈H₄₀O₄: C 81.45, H 7.20, O 11.42; found C 81.36, H 7.26, O 11.52.

Acknowledgements

We thank Dr. Les Gelbaum for assistance with NMR, Mr. David Bostwick for mass spectra, and Dr. Kenneth Hardcastle of Emory University for collection and assignment of the crystal structure for compounds **4** and **8**. This work was supported in part by the U.S. National Science Foundation (Grants No. ECS-437925 and CHE-1300497).

Keywords: density functional calculations \cdot noncovalent interactions \cdot pi interactions \cdot stacking interactions \cdot substituent effects

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Received: June 18, 2015 Published online on November 16, 2015

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