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Heterotriangulenes—Structure and Properties

Jason E. Field and D. Venkataraman*

Department of Chemistry,
University of Massachusetts, 710 N. Pleasant Street,
Amherst, Massachusetts 01003

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Well-ordered electroactive molecules are emerging as potential candidates for many material science applications. Molecular symmetry requirements, such as planarity or chirality, are inherent for achieving such molecular ordering, which in turn may give rise to interesting electronic and/or optical properties.[1] For example, planar electroactive molecules forming columnar stacks have found potential application as molecular wires[2] and in solar cells.[3] Similarly, helicene derivatives have been observed to form helical columnar motifs.[4] Such structures are potential candidates for nonlinear optical and circularly polarized light (CPL) emitting materials. We recently set out to synthesize the high-symmetry molecules **1** and **2**, which are based on triphenylamine—a moiety that has been widely exploited for its physical and electronic properties in display applications.[5] These molecules are related to a class of compounds termed as triangulenes;[6] however, unlike triangulenes, there is relatively little information regarding the solid-state structure and properties of **1** and **2**.[7] As a first step in developing well-ordered materials, the solid-state structure of the constituent molecule must be established. It is in this regard that we report the crystal structures, electrochemical properties, and photochemical properties of the planar molecule **1** and the C_2 symmetric molecule **2**.

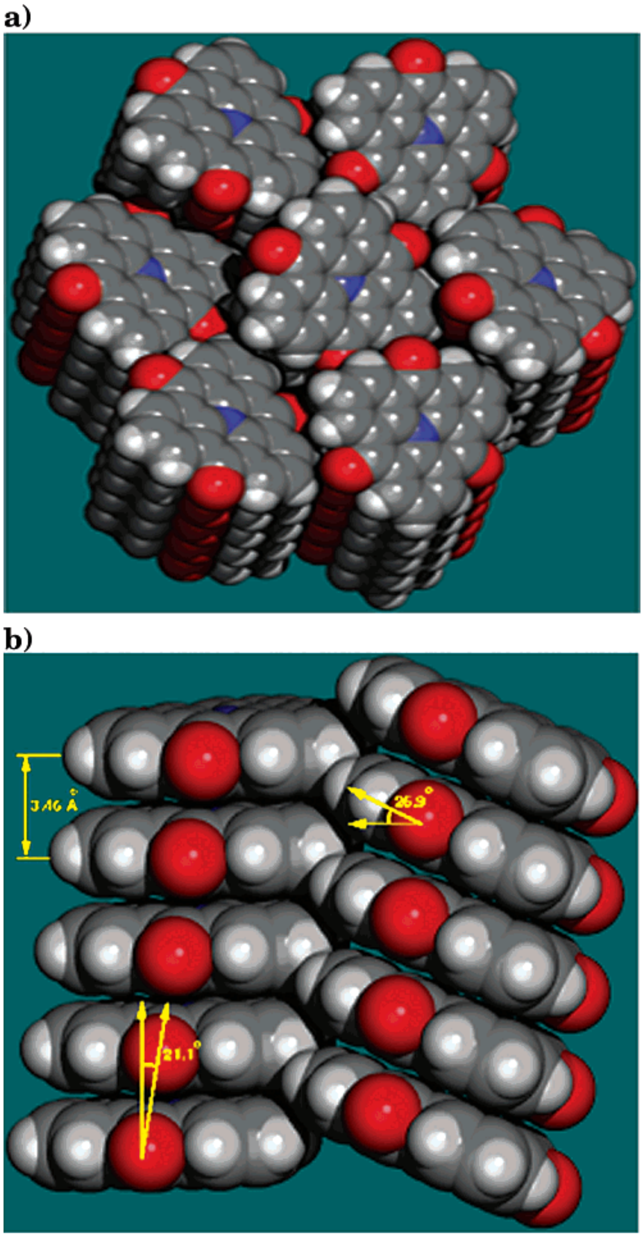

Figure 1. Illustration of (a) the packing motif and (b) the stacking interactions in the single-crystal X-ray structure of **1**.

The previously reported synthesis[7] was modified to obtain **1** and **2** in improved yields.[8] From the single-crystal X-ray structure of **1** shown in Figure 1, it can be seen that the molecules are planar with D_{3h} symmetry and are densely packed (Kitaigorodskii packing coefficient = 0.72) in columnar π-stacks along the *a*-axis.[9] Within each π-stack, the molecules are 3.46 Å apart with an offset angle of 21.1°. Between the stacks,

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* To whom correspondence should be addressed. E-mail: dv@chem.umass.edu.

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[8] See Supporting Information.

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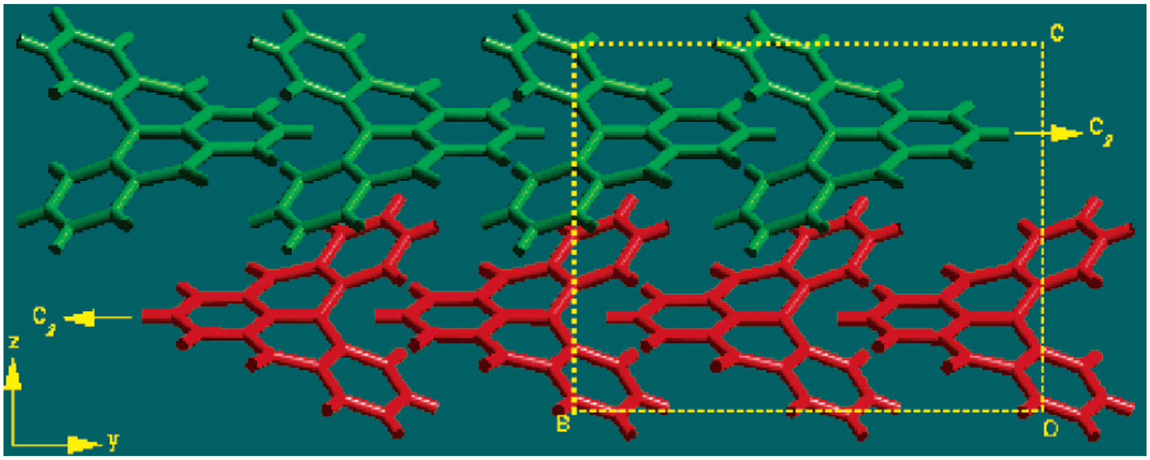
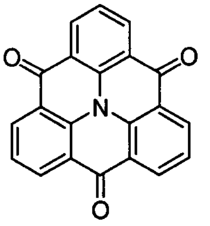


Figure 2. View along the *a*-axis in the single-crystal X-ray structure of **2**; separate atropisomers are shown in green and red.

the molecules have a herringbone-type arrangement with an angle of 26.9° between the planes. This packing is quite reminiscent of many molecular-based conductors, such as perylene.[10] The planar geometry and 3-fold symmetry make **1** an ideal conjugated, electroactive building block for 3- and (3, *n*)-connected electronic networks and discotic electroactive liquid-crystalline phases.[2]

In comparison, without a third bridging carbonyl, **2** adopts a nonplanar geometry and is of C_2 symmetry. The crystal structure clearly shows that **2** exists as a racemic mixture of atropisomers (Figure 2).[11] The packing of this molecule is akin to that of the β-structures found in polynuclear aromatic hydrocarbons.[12] The molecules pack as columnar stacks along the *a*-axis. These stacks interdigitate into rows along the *b*-axis. The C_2-axes of the molecules are parallel to the *b*-axis. Since the net molecular dipole moment is expected be along the C_2-axis, the rows pack such that the dipole moment vectors are opposed to each other. When viewed edge-on, in a direction perpendicular to the C_2-axis, the interplanar angle between the terminal rings is 45°. In comparison, this angle is 58° in helicenes and ~70° in binaphthyl. This C_2-symmetry of **2** makes it an ideal building block for conjugated helical structures[13] as well as a candidate for constructing CPL emitting materials.[14]

We investigated the photochemical and electrochemical properties of **1** and **2** and for comparison phenylacridone (**PHA**) (Figure 3). The absorption and emission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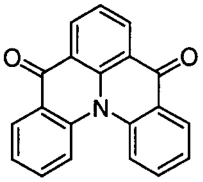
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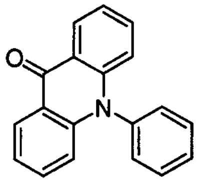
PHA

spectra were collected in CH_2Cl_2/10% trifluoroacetic acid (TFA) because **1** had excellent solubility in this mixture. The absorption maxima (λ_{max}) of **1**, **2**, and **PHA** are 422, 458, and 412 nm, respectively. When excited at these wavelengths, **1**, **2**, and **PHA** emit 499 nm (green), 540 nm (yellow), and 471 nm (blue). The red shift in the emission of **2** from **PHA** can be attributed to the increased conjugation in the chromophore; however, this argument fails to explain the lack of a further red shift in the emission of **1**. This phenomenon may be attributed to differential protonation or an electronic transition from lower lying orbitals.[15] The quantum yield of **2** (λ_{max} = 435 nm) was measured to be 0.42 in benzene with reference to perylene (λ_{max} = 440 nm).

Since the spectra were collected in an acidic medium, they are likely to correspond to a protonated or partially protonated state. It has been hypothesized that such a protonation occurs at the carbonyl oxygen rather than the heterocyclic nitrogen.[4a,16] By comparing the spectral data to that of **2** and **PHA** in CH_2Cl_2 without TFA, the

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(9) Crystal and refinement data for **1**: Monoclinic, $P2_1/n$ (14), a = 3.894(3) Å, b = 18.039(2) Å, c = 19.303(2) Å, β = 92.20(3)°, V = 1355.3 (2) Å^3, Z = 4, ρ = 1.584, μ = 0.11 mm^{-1}. Single-crystal data collected were collected on a Nonius kappaCCD system at room temperature using Mo Kα (λ = 0.71073 Å) radiation. The structure was solved using SIR92 and was refined by full-matrix least-squares on F_o^2 using SHELXL 97 (data/parameters: 1245/226), converging to R_1 = 0.062, wR_2 = 0.1536 (on 767, $I > 2\sigma(I)$ observed data); R_1 = 0.1194, wR_2 = 0.2082 (all data).

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(11) Crystal and refinement data for **2**: Monoclinic, $C2/c$ (15), a = 9.232(2) Å, b = 13.508(4) Å, c = 10.764(3) Å, β = 91.33(1)°, V = 1342.09 (6) Å^3, Z = 4, ρ = 1.471, μ = 0.096 mm^{-1}. Single-crystal data collected were collected on a Nonius kappaCCD system at room temperature using Mo Kα (λ = 0.71073 Å) radiation. The structure was solved using SIR92 and was refined by full-matrix least-squares on F_o^2 using SHELXL97 (data/parameters: 1524/106), converging to R_1 = 0.0392, wR_2 = 0.1057 (on 1371, $I > 2\sigma(I)$ observed data); R_1 = 0.0447, wR_2 = 0.1129 (all data).

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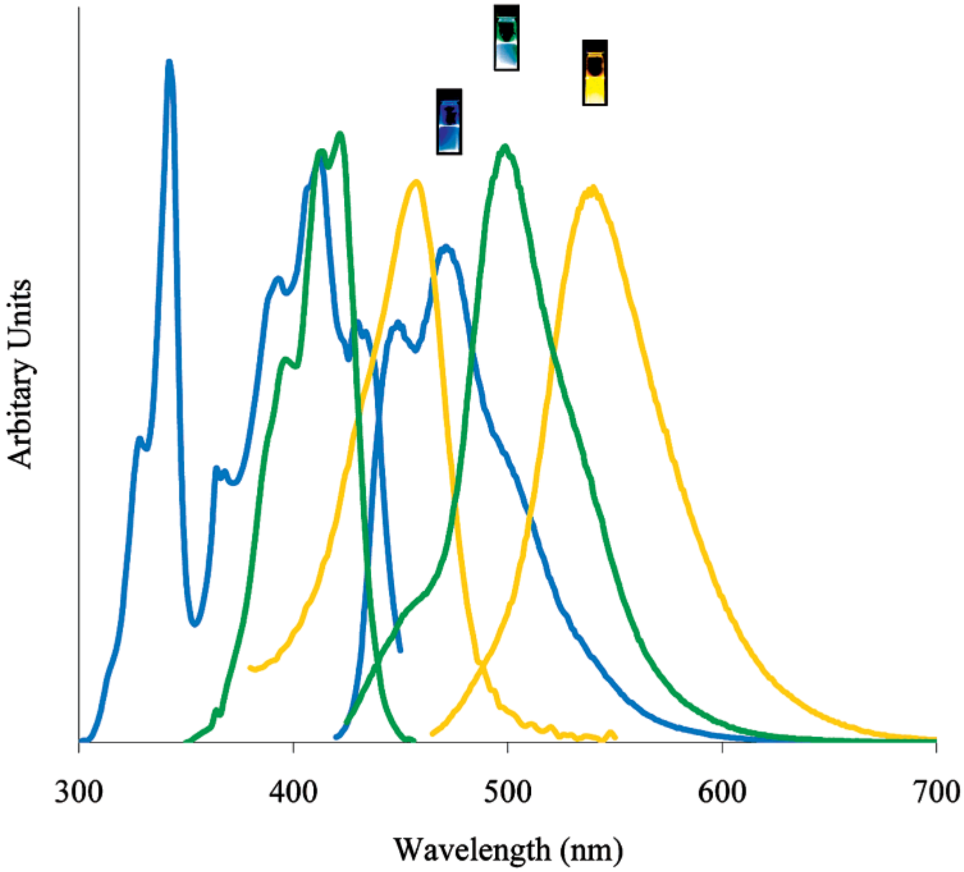

Figure 3. Absorption and emission spectra of compounds **1** (green), **2** (yellow), and **PHA** (blue). Inset pictures are photographs of actual compounds (10^{-3} M in 10% TFA/CH_2Cl_2) exposed to 365-nm light.

effect of protonation appears to be a red shift in the range of 15−75 nm.

Cyclic voltametry of **2** and **PHA** show irreversible oxidation potentials (vs SCE) at 0.92 and 0.98 V as compared to that of triphenylamine at 1.01 V. The oxidation potential of **1** was not obtained due to its low solubility in suitable organic solvents.

In summary, we have reported the solid-state structures and photophysical properties of **1** and **2** as well as electrochemical properties of **2**. The solid-state packing of **1** is reminiscent of the stacking motifs found in many molecular conductors and it would be of interest to study the electronic properties of these compounds upon oxidation. The luminescence properties of **1** and **2** make them potential candidates for electroluminescent materials. The C_2-symmetry of **2** may be exploited for the construction of CPL emitting materials for backlighting in LCDs. Our focus now is the synthesis of functionalized derivatives of **1** and **2** to systematically develop them as practical electroactive materials.

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Supporting Information Available: Experimental procedures and characterization data (PDF) and crystallographic information files (CIF) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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