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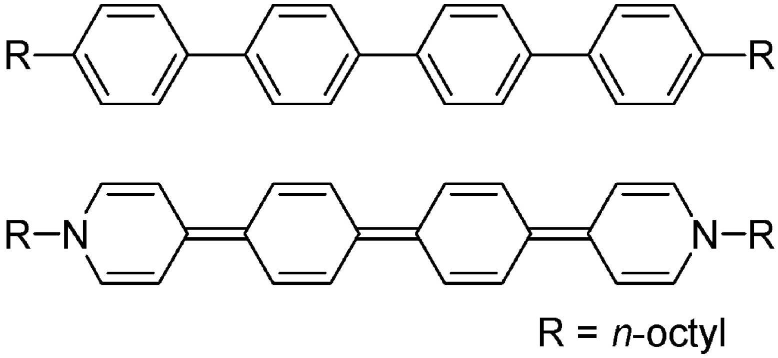

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Synthesis and Characterization of a Highly Reducing Neutral “Extended Viologen” and the Isostructural Hydrocarbon 4,4′′′′-Di-*n*-octyl-*p*-quaterphenyl

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Abstract: The molecule 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl was synthesized in one step by a nickel-catalyzed cross-coupling reaction. Powder X-ray diffraction shows that it crystallizes in a layered structure with the long axis of the molecule nearly perpendicular to the layer plane. Differential scanning calorimetry indicates a transition to a liquid−crystalline phase at 81 °C. Reaction of 4,4′-bis(4-pyridyl)biphenyl with 1-bromooctane yields the dication **2**$^{2+}$ 2Br$^-$, an “extended viologen” isostructural with 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl. Reduction of **2**$^{2+}$ 2Br$^-$ with sodium amalgam in DMF yields **2**, the first neutral extended viologen to be isolated. The molecule **2** is, to the best of our knowledge, the most reducing neutral organic molecule that has been synthesized. Single-crystal X-ray diffraction shows that a diradical form, either singlet or triplet, makes an important contribution to the electronic structure of **2**. The broadened ^{1}H NMR spectrum of **2** indicates the presence of a triplet, but it has not been possible to observe the triplet by ESR spectroscopy. The electronic structure of **2** appears to be closely related to that of a classic molecule, Chichibabin’s hydrocarbon.

Introduction

We recently examined the neutral form of phenyl viologen (Figure 1b, R = H) as an isostructural n-dopant for *p*-quaterphenyl (Figure 1a, R = H).[1] An isostructural n-dopant is a molecule that has the same skeletal structure as a molecular semiconductor (*p*-quaterphenyl in this case) but has one or more carbon atoms replaced by nitrogen, analogous to the replacement of some silicon atoms by phosphorus in n-doped silicon. The dopant thus formed must be neutral in charge and a good electron donor. When a small amount of the isostructural n-dopant is cocrystallized with the host molecular semiconductor it will, ideally, donate electrons to the semiconductor and thus n-dope it. Because the dopant is isostructural with the semiconductor molecule, it will cocrystallize substitutionally and therefore will be spatially fixed within the crystal lattice, which means that isostructurally doped molecular semiconductors will be able to support the space-charge regions that are essential components of traditional inorganic semiconductor devices.[2] We found, however, that neutral phenyl viologen is not a sufficiently strong electron donor to act as a dopant in *p*-quaterphenyl. That finding has led us to the current investigation, in which we have synthesized a neutral “extended viologen” (**2** in Figure 1c). When a standard viologen in its neutral form gives up two electrons to form a dication, two quinoid rings are converted to aromatic rings (see Figure 1b), providing the driving force for the reaction and making a neutral viologen a strong electron donor. When the neutral extended viologen **2** in Figure 1c gives up two electrons, four quinoid rings become aromatic, presumably providing a stronger driving force and making it a stronger electron donor than a standard neutral viologen.

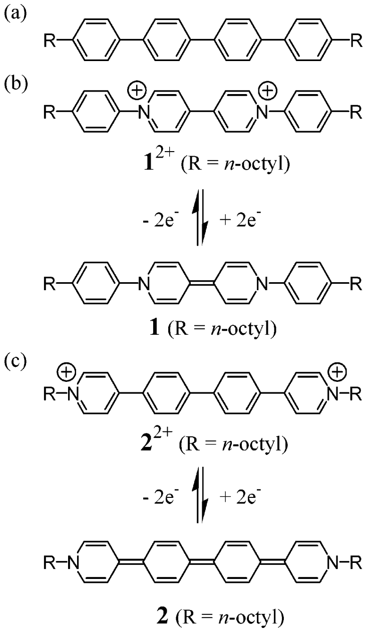

Figure 1. (a) *p*-Quaterphenyl (R = H), 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl (R = *n*-octyl); (b) phenyl viologen (R = H), 1,1′-bis(4-*n*-octylphenyl)-4,4′-bipyridinium (R = *n*-octyl); (c) extended viologen **2** and its dication **2**$^{2+}$.

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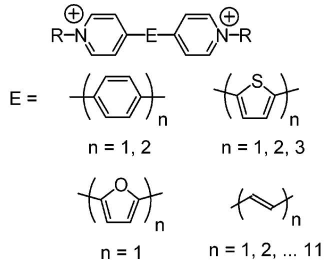


Figure 2. Known extended viologens.

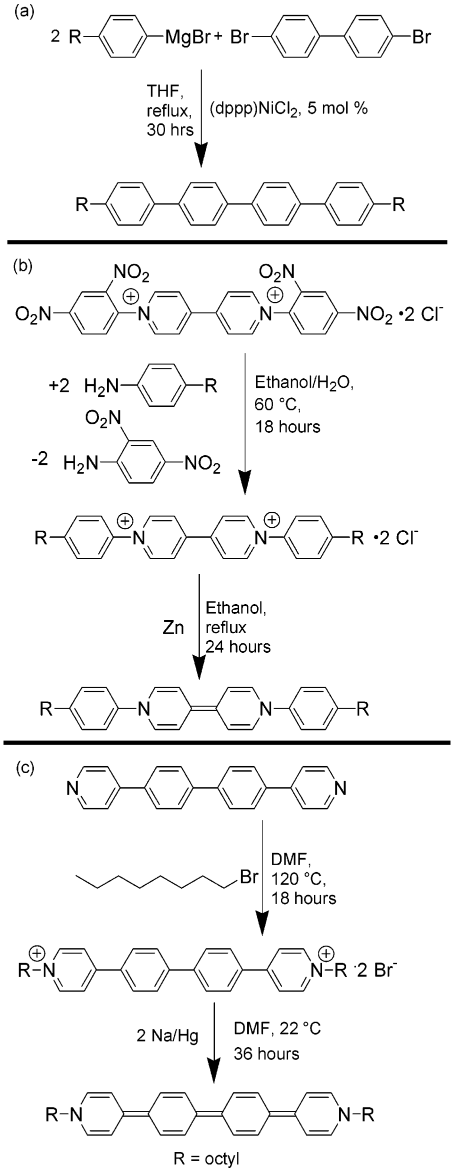
The molecular semiconductor we have chosen to investigate is 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl, shown in Figure 1a. While α,*ω*-dialkyloligothiophenes have been thoroughly examined as components of field-effect transistors,[3−5] similarly functionalized oligophenylenes are virtually unexplored. The octyl groups of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl increase its solubility and also make it possible to create an isostructural extended viologen, **2** in Figure 1c. We have also examined the standard viologen 1,1′-bis(4-*n*-octylphenyl)-4,4′-bipyridinium, $\mathbf{1}^{2+}$ (Figure 1b), and its neutral form **1** in order to contrast it with **2**. The molecules **1** and **2** are isomers and have the same skeletal structure; the only difference between the two is that the positions of two carbon atoms and two nitrogen atoms have been interchanged. Yet we expect **2** to be a stronger reducing agent than **1**.

There are several known molecules in which two pyridylium rings are connected by a *π*-conjugated fragment (Figure 2), and all of these can be considered extended viologens. Dications that have phenylene,[6−8] thiophene,[6,9,10] furan,[6] and polyene[11−13] units between the pyridylium rings have been synthesized. Electrochemical studies of several of those derivatives have been performed, but no extended viologen of any kind has been isolated as a neutral molecule. Herein we report the synthesis, isolation, and characterization of the neutral extended viologen **2**, which we believe is the most reducing neutral organic molecule that has been isolated to date. The molecule **2** also has an interesting electronic structure, closely related to Chichibabin's hydrocarbon,[14] as will be discussed below.

Results and Discussion

Synthesis and Spectroscopy. Syntheses are outlined in Scheme 1. The synthesis of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl is a straightforward nickel-catalyzed cross-coupling reaction[15] between 4-*n*-octylphenylmagnesium bromide and 4,4′-dibromobiphenyl. Its UV−vis absorption at 304 nm corresponds to a HOMO−LUMO gap of 4.1 eV, similar to the value determined electrochemically (see below).

Scheme 1. Synthesis of (a) 4,4′′′′-Di-*n*-octyl-*p*-quaterphenyl, (b) $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ and **1**, and (c) $\mathbf{2}^{2+}\,2\mathrm{Br}^-$ and **2**.



The viologen $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ was prepared by a reaction that has been previously employed for the synthesis of phenyl viologen[16] and other aryl viologens. The reaction of 1,1′-bis(2,4-dinitrophenyl)-4,4′-bipyridilium dichloride (obtained from the reaction of 4,4′-bipyridine with 1-chloro-2,4-dinitrobenzene) with 4-*n*-octylaniline yields $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ and 2 equiv of 2,4-dinitroaniline. The reaction proceeds by a nucleophilic attack by the aniline nitrogen on a carbon α to the nitrogen of the pyridinium ring, resulting in an opening of the pyridinium ring, which is followed by ring closing with release of 2,4-dinitroaniline.[17] The ring-

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opening and ring-closing reactions occur with a variety of para-substituted anilines,[18] and the method therefore should be applicable to the synthesis of a variety of aryl viologens. Recrystallization of $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ from ethanol/ethyl acetate without the exclusion of water results in the dihydrate $\mathbf{1}^{2+}\,2\mathrm{Cl}^-\cdot 2\mathrm{H_2O}$. The spectroscopy of $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ is similar to that reported for phenyl viologen dichloride.[1] The chloride was converted to the hexafluorophosphate to improve its solubility in THF for electrochemical measurements.

Reduction of $\mathbf{1}^{2+}\,2\mathrm{Cl}^-$ by zinc in ethanol yields dark red **1**, which can be recrystallized as thin plates from hot toluene. Crystals of **1** maintain their dark red color for extended periods in air, but red solutions of **1** rapidly turn deep green upon exposure to air. Spectroscopy is similar to that of the reported neutral phenyl viologen.[1]

The extended bipyridine 4,4′-bis(4-pyridyl)biphenyl was synthesized by a slightly modified literature method[19] in which we used 4-iodopyridine in place of 4-bromopyridine.[20] Its reaction with 1-bromooctane in DMF yields $\mathbf{2}^{2+}\,2\mathrm{Br}^-$. An extended viologen similar to $\mathbf{2}^{2+}$ with methyl groups in place of the octyl groups has been reported,[7] and like that methyl derivative, $\mathbf{2}^{2+}$ is highly fluorescent. When $\mathbf{2}^{2+}\,2\mathrm{Br}^-$ in ethanol is excited at 348 nm it emits light at 427 nm with a quantum yield of 0.95, determined versus an anthracene standard.[21]

The neutral extended viologen **2** is synthesized by the sodium amalgam reduction of $\mathbf{2}^{2+}\,2\mathrm{Br}^-$ in DMF. The reagent $\mathbf{2}^{2+}\,2\mathrm{Br}^-$ has low to moderate solubility in DMF at room temperature, while **2** has essentially none, so the product crystallized from the reaction mixture as the reaction proceeded. The product **2** can be purified by recrystallization from hot pyridine. Spectroscopy and further characterization of **2** are discussed below.

Electronic Structure of 2.

i. NMR. The first indication that **2** has an unusual electronic structure came from its ^{1}H NMR spectrum, taken in pyridine-d_5 at 90 °C (see Supporting Information). A resonance for the methyl group (of the octyl chain) is observed at 0.92 ppm, five of the methylenes are overlapping at 1.30 ppm, and it appears that the two remaining methylenes give rise to a resonance at 1.5 ppm and a broadened resonance at 6.4 ppm. There are no observable resonances for the protons on the quinoid rings. The identity of **2** was checked by oxidizing a sample with $\mathrm{I_2}$, which yielded a compound with a ^{1}H NMR spectrum consistent with $\mathbf{2}^{2+}\,2\mathrm{I}^-$. It is unlikely that the broadened and shifted ^{1}H NMR of **2** is due to adventitious oxidation of a small fraction of **2** to $\mathbf{2}^{+}$ or $\mathbf{2}^{2+}$ and fast electron exchange of the cation or dication with neutral **2**. There are two reasons that adventitious oxidation is an unlikely cause: (a) ^{1}H NMR spectra of different samples of **2**, including ones from different preparations, are identical. Adventitious oxidation would presumably occur to varying extents and therefore cause varying amounts of broadening and paramagnetic chemical shifts. (b) ^{1}H NMR spectra of quinoid **1**, which is also very air-sensitive in solution and would also quantitatively react with any $\mathrm{O_2}$ present, are always sharp and complete. Spectra of **1** and **2** were obtained under similar conditions (in hot pyridine-d_5) and were prepared in the same glovebox. It is most likely that the ^{1}H NMR spectrum of **2** indicates the presence of unpaired electrons on the ring system of **2** that are intrinsic to neutral **2**, and that was investigated further.

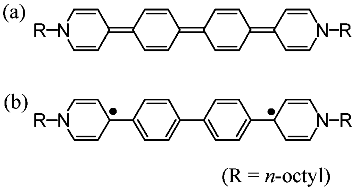

Figure 3. (a) Closed-shell, quinoid form of **2**. (b) Diradical (singlet or triplet) form of **2**.

ii. Resonance Structures, Spin State, and Calculations. Two resonance structures for **2** that should be considered are shown in Figure 3. Figure 3a is the closed-shell, fully quinoid structure that might be expected to be a good representation of the electronic structure of **2**. In standard neutral viologens, for example, the spectroscopic properties and bond lengths from X-ray crystallography are in full agreement with a quinoid structure.[1,22] However, if one imagines a neutral extended viologen with a very long chain of phenylene rings, it becomes clear that at some point the energetic stabilization gained by converting a long chain of quinoid rings to aromatic rings will be greater than the energy lost by breaking one π-bond, and a diradical of the type shown in Figure 3b will become favored over the fully quinoid structure. (In fact, in extended quinone systems that consist of four rings a diradical structure is in equilibrium with the quinoid structure, while three-ring and smaller systems are quinoid and the five-ring system is almost completely diradical.[23,24]) It appears that in the four-ring system of **2** the diradical resonance structure makes an important contribution to the electronic structure.

The diradical of Figure 3b can represent two different spin states of the molecule: a singlet diradical or a triplet diradical. The singlet diradical shown in Figure 3b, along with other diradical resonance structures, would be a resonance structure with the quinoid form of the molecule, and their weighted average would describe the electronic structure of the singlet state of the molecule. However, a singlet diradical should not exhibit the broadened and shifted ^{1}H NMR resonances observed for **2**. On the other hand, it is possible that another spin state of **2**, a triplet diradical, is thermally accessible and is in equilibrium with the singlet and causes the broadening of the ^{1}H NMR.

Density functional calculations of **2** (with methyl groups substituted for the octyl groups) were performed with Gaussian 03[25] at the UB3LYP/6-31G* level. If the spin state of **2** is set to a singlet, geometry optimization yields a structure in which all the rings are coplanar and the molecular orbitals are consistent with the quinoid structure of Figure 3a. If the optimization is started with the two outer rings twisted at 90° relative to the inner rings, the first several cycles of the optimization resemble a singlet diradical in which there is unpaired spin density at both ends of the molecule. However, as the geometry is optimized, the outer rings twist into the configuration where all the rings are coplanar and the electronic structure converts to the quinoid form. A calculation that

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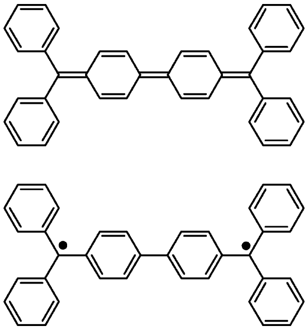

Figure 4. (a) Closed-shell, quinoid form of Chichibabin's hydrocarbon. (b) Diradical (singlet or triplet) form of Chichibabin's hydrocarbon.

included the command "guess = mix", which allows the mixing of the quinoid and singlet diradical structures, was unstable and did not find a minimum. A multireference theoretical method such as CASSCF would be appropriate for further study of **2** in the singlet state. If the spin state of **2** is instead set to a triplet, the minimized structure has a twist of 33° between the two inner rings and a twist of 18° between the outer and inner rings. Also, the bond distances in the triplet are closer to what would be expected in a diradical structure. Interestingly, the energy of the minimized triplet diradical is calculated to be 1.0 kcal/mol *lower* in energy than the minimized closed-shell singlet. More evidence for the triplet state was sought in the ESR spectrum.

iii. ESR. A singlet diradical should display no ESR spectrum, while a triplet diradical has a distinctive ESR signature.[26] As a dilute solution in 1,4-dioxane, **2** exhibited no ESR signal. However, when the solution was frozen at 0 °C, a single resonance at $g = 2.0$ was observed, indicating the presence of a monoradical. In one trial its peak-to-peak width (of the derivative spectrum) was 2 G, and in another trial it was 10 G. The powder spectrum had a similar resonance at $g = 2.0$ with a peak-to-peak width of 10 G. In no case was a signal observed at half the usual magnetic field, where the $\Delta M_s = 2$ transition of a triplet is expected, nor were the additional resonances around $g = 2.0$ due to the zero-field splitting of a triplet observed. The doublet (monoradical) signal may originate from the one-electron reduction of impurities by **2**, but it is surprising then that the signal is not observed in the room-temperature solution in dioxane.

The ESR results for **2** are puzzling, especially in light of the solution-phase ^{1}H NMR spectrum, which seems to indicate the presence of a thermally accessible triplet. However, there is a molecule with an electronic structure that appears to be closely related to that of **2**, and its ESR spectra have been equally perplexing. The molecule is Chichibabin's hydrocarbon (Figure 4), first reported in 1907.[14] Both Chichibabin's hydrocarbon and **2** can be written as closed-shell singlets with their two central rings in a quinoid form, or they can be written as diradicals with two aromatic central rings. The electronic state of Chichibabin's hydrocarbon (singlet, triplet, or an equilibrium mixture of the two) was a subject of study for decades, mainly by ESR spectroscopy.[27,28] References 27 and 28 summarize the results of those investigations and give relevant references. Solution-phase ESR spectra of Chichibabin's hydrocarbon always display a signal due to a monoradical, probably due to dimerization of the diradical or reaction of one end of the diradical with adventitious impurities. ESR studies of powdered samples by Brauer showed the presence of a triplet, and the conclusion of those investigations was that the singlet and triplet were in thermal equilibrium with the triplet 5.5 kcal/mol higher in energy than the singlet.[29−31] However, later attempts to observe the triplet ESR signal of Chichibabin's hydrocarbon were unsuccessful.[28]

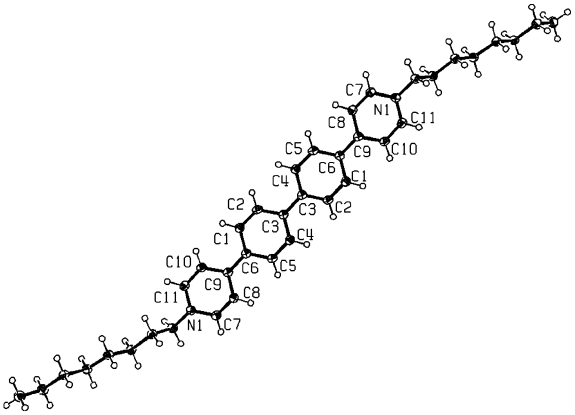

Figure 5. ORTEP representation of **2**.

iv. X-ray Crystal Structure of 2. Crystal data is given in the Supporting Information. Single crystals of **2** were grown by slow cooling of a hot pyridine solution. In solution, **2** is blue, while the crystals are metallic green. Interestingly, but probably coincidentally, Chichibabin's hydrocarbon forms similar blue-violet solutions and metallic green crystals.[28] Single-crystal X-ray diffraction revealed the structure shown in Figure 5. All four of the rings are coplanar. There is a slight pyramidalization at the nitrogens, so that the nitrogen−methylene bond is at a 9° angle to the plane of the rings. It is the bond lengths in **2** that lend the most insight into its electronic structure. Table 1 lists selected bond lengths of **2** along with relevant bond lengths from other compounds for comparison. The analogous bonds lengths are given for neutral methyl viologen[22] (which has a fully quinoid structure), phenyl viologen dication[1] (in which both rings are aromatic), and phenyl viologen radical cation[1] (which is an average of the quinoid and aromatic resonance structures). The central C(3)−C(3) bond of **2**, for example, at 1.438(3) Å, is distinctly longer than the central double bond of neutral methyl viologen at 1.363(9) Å and shorter than the single bond of phenyl viologen dication at 1.485(3) Å. It is closest in length to phenyl viologen radical cation's central bond at 1.427(4) Å. A similar pattern is seen throughout the central two rings of **2**. If one assumes that a closed-shell singlet electronic structure would yield the normal pattern of alternating single and double bond lengths, then the overall set of bond lengths implies a contribution of at least 50% from the singlet diradical resonance form shown in Figure 3. It seem unlikely that in the solid state, where all the rings are coplanar, that the triplet state is occupied to any significant degree. The similarity of the bond lengths of **2** and those of

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Table 1. Comparison of Bond Lengths in **2**, Chichibabin's Hydrocarbon,[28] Neutral Methyl Viologen,[22] Phenyl Viologen Radical Cation,[1] Phenyl Viologen Dication,[1] and the Calculated (UB3LYP/6-31G*) Optimized Structure of **2**

	distance (Å)					
bond	**2** (X-ray)	Chichibabin's Hydrocarbon	Methyl Viologen^0	Phenyl Viologen$^+$	Phenyl Viologen^{2+}	**2** (calcd)
C(3)−C(3)	1.438(3)	1.448(4)	1.363(9)	1.427(4)	1.485(3)	1.428
C(2)−C(3)	1.421(2)	1.420(3)	1.461(6)	1.422(4)	1.396(2)	1.435
C(3)−C(4)	1.425(2)	1.420(3)	1.444(7)	1.424(4)	1.391(2)	1.435
C(1)−C(2)	1.360(2)	1.371(3)	1.325(8)	1.348(4)	1.374(2)	1.369
C(4)−C(5)	1.361(2)	1.372(3)	1.336(8)	1.349(4)	1.376(2)	1.369
C(5)−C(6)	1.426(2)	1.429(3)				1.437
C(1)−C(6)	1.427(2)	1.424(3)				1.437
C(6)−C(9)	1.416(2)	1.415(3)				1.414
C(8)−C(9)	1.441(2)					1.447
C(9)−C(10)	1.432(2)					1.447
C(7)−C(8)	1.347(2)					1.357
C(10)−C(11)	1.346(2)					1.357
C(11)−N(1)	1.3800(19)					1.386
N(1)−C(7)	1.3699(19)					1.386

Chichibabin's hydrocarbon is striking. For that molecule it was estimated that the contribution from the diradical resonance form is about 60%.[28] The final column of Table 1 lists the bond distances of the minimized structure from the density functional calculations referred to above, with the spin state of **2** set to a singlet. Although the calculated HOMO of **2** looks exactly as would be expected for a fully quinoid structure (see Supporting Information) and there is no indication of a singlet diradical, the calculated bond distances are in reasonable agreement with the experimental values.

v. Summary. The electronic structure of **2** is somewhat perplexing, with its ^{1}H NMR spectrum indicating the presence of at least some triplet diradical (and DFT calculations reinforcing the possibility, with the triplet state at a energy comparable to the singlet), yet no triplet could be detected in the ESR spectrum. X-ray crystallography indicates some singlet diradical contribution to the electronic structure of **2** in the solid state. The classic molecule Chichibabin's hydrocarbon is closely related to **2**, and further investigation of both by ESR spectroscopy and modern electronic structure calculations may be warranted.

Electrochemistry. As explained in the Introduction, our original motivation for the synthesis of **2** was our belief that it would be a stronger reducing agent than a regular viologen such as **1**. That hypothesis was tested by solution-phase electrochemical measurements. Cyclic voltammograms of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl, $\mathbf{1}^{2+}\,2\mathrm{PF_6}^-$, and $\mathbf{2}^{2+}\,2\mathrm{PF_6}^-$ as saturated solutions in THF are shown in Figure 6. All are referenced to ferrocene$^{0/+}$ at 0 V. Two reversible, one-electron reductions of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl occur at −2.83 and −3.05 V, and a nonreversible oxidation was observed at approximately +1.2 V. Two reversible, one-electron reductions of $\mathbf{1}^{2+}$ occur at −0.70 and −1.00 V. The two compounds exhibit electrochemical behavior very similar to that of their respective parent compounds, *p*-quaterphenyl and phenyl viologen.[1] One reversible, two-electron reduction (or two very closely spaced one-electron reductions) of $\mathbf{2}^{2+}$ occurs at −1.48 V followed by two reversible, one-electron reductions (to $\mathbf{2}^-$ and $\mathbf{2}^{2-}$) at −2.49 and −2.86 V. The fact that the reduction of $\mathbf{2}^{2+}$ to **2** appears to occur in a single, two-electron step makes sense in the light of the greater spatial separation (and decreased interaction) of the pyridinium moieties compared to **1**. Single-potential, two-electron reductions and oxidations of organic molecules tend to occur for larger molecules and for those that undergo a structural rearrangement in one or both electron-transfer steps.[32]

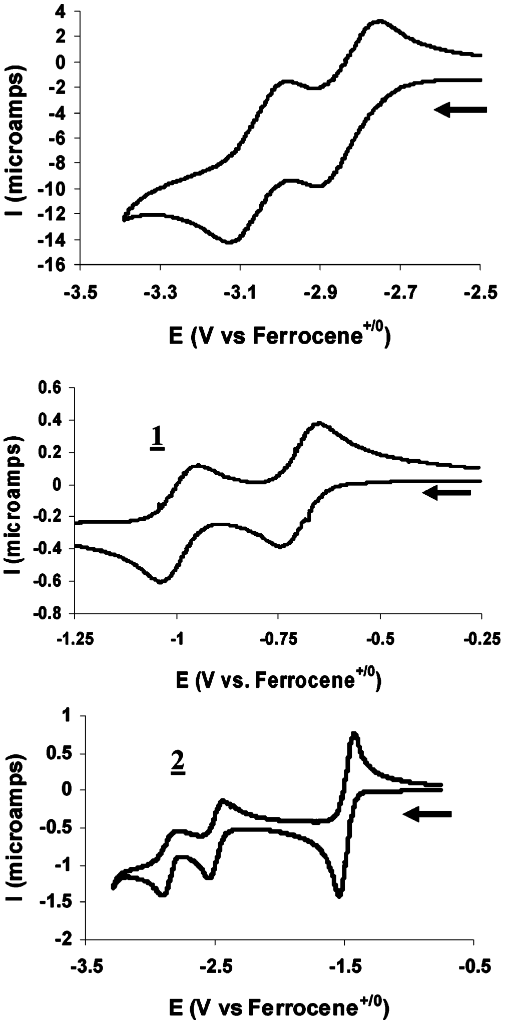

Figure 6. Cyclic voltammetry of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl (top), **1** (middle), and **2** (bottom). All in THF, with potentials relative to ferrocene$^{0/+}$.

The electrochemical data can be combined to create an approximate picture of the solid-state energy levels of 4,4′′′′-

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(32) Evans, D. H.; Hu, K. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3983−3990.

di-*n*-octyl-*p*-quaterphenyl doped with **1** or **2**. The difference between the reduction and oxidation potentials of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl indicate that as a molecular solid it had a band gap of approximately 4.0 eV. Cocrystallization of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl with a small amount of **1** would create a donor level about 1.8 eV from the conduction band of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl (from redox potentials 2.83−1.00 V). While **2** is a better electron donor than **1** by 0.48 V (−1.48 V versus −1.00 V), it will create a donor level in 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl that is still about 1.3 eV from the conduction band, so **2** is not expected to function as an electron donor in 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl.

Our attempt to create a good electron donor in **2** was successful in that it is a better donor than the highly reducing neutral viologen **1** by 0.48 V. In fact, to the best of our knowledge, **2** is the most reducing neutral organic molecule yet synthesized. The reducing strength of a molecule can be judged by its (0/+) redox potential. There are transition metal organometallic complexes, such as the permethylated, 19-electron FeCp*(η^6-C_6Me_6) and CoCp*$_2$ (Cp* = η^5-C_5Me_5), that are stronger reducing agents, with (0/+) redox potentials of −2.30 V (vs Fc$^{0/+}$, in DMF) for FeCp*(η^6-C_6Me_6) and −1.94 V (vs Fc$^{0/+}$, in CH_2Cl_2) for CoCp*$_2$.[33] The (0/2+) potential of −1.48 V for **2** puts its reducing strength between that of CoCp*$_2$ and CoCp$_2$. There are also organic anions that are more reducing than **2**: naphthalene has a (0/−) couple of −3.10 V (vs Fc$^{0/+}$, in THF),[33] so sodium naphthalide is an extremely strong reductant. But among neutral organic molecules, **2** appears to be the strongest electron donor.

Solid-State Conductivity of 1 and 2. Although our main interest in **1** and **2** was their possible utility as dopants for 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl, our finding that neutral phenyl viologen is an electrical conductor as a pure material[1] led us to examine the solid-state conductivity of **1** and **2**. Measurements were carried out as described previously.[1] Because these were two-point measurements, a series of sample masses for each substance was measured to examine the influence of contact resistance. The cross-sectional area of the pressed pellets in the apparatus is constant, so the thickness of the sample, and therefore its measured resistance, will increase in direct proportion to the sample mass if the contact resistance is not significant. At each mass, the same sample was repacked and measured for a total of four measurements. Current was measured as a function of applied potential from 0 V to +2 V to −2 V to 0 V.

Figure 7 shows the results for **1**. Each current−voltage plot in the top graph is the average of the four runs at each mass; all of them are linear, indicating Ohmic behavior. The inverse of the slope of each plot (obtained by linear regression) is the resistance. The resistance as a function of mass is shown in the bottom graph. The horizontal error bars represent the estimated weighing error, and the vertical error bars are the standard deviation over the four measurements at each mass (representing, essentially, the variation due to sample packing). Extrapolation of a least-squares-fit line to zero mass yields the contact resistance, which is a very small negative number (−35 kΩ), which for the remaining calculations is assumed to be zero. The conductivity of **1** was calculated by assuming a density of 1.18 g/cm^3 and using the known cross-sectional area of the sample disk (0.317 cm^2) to calculate the sample thickness. An average conductivity of 4.3 × 10^{-8}(0.6 × 10^{-8}) Ω^{-1} cm^{-1} was calculated from 20 measurements (four times each on five samples).

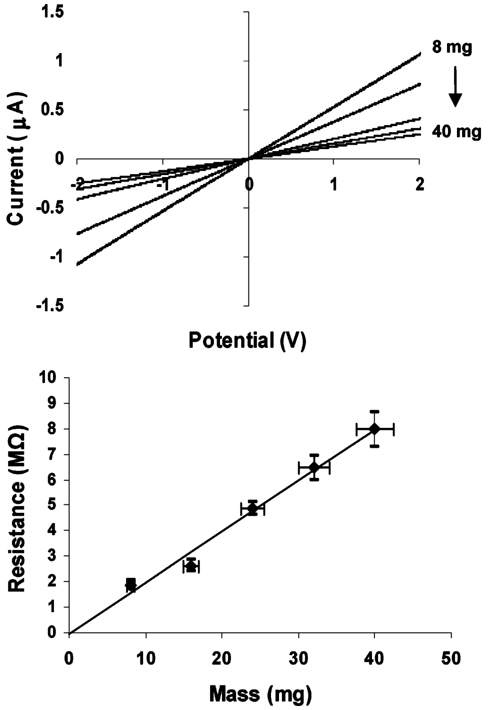

Figure 7. Current−voltage plots for pressed polycrystalline samples of **1**, mass 8, 16, 24, 32, and 40 mg (top). Measured resistance of the five samples, with a best-fit line extrapolated to zero mass to yield the contact resistance (bottom).

Current−voltage plots for **2** are qualitatively similar to those of **1** and are given in the Supporting Information. The data were treated in the same manner as that for **1**. In this case the contact resistance is 26 kΩ, which was subtracted from all measured resistances for calculation of the conductivity. The density calculated from the crystal structure (1.176 g/cm^3) was used to calculate sample thicknesses. An average conductivity for **2** of 9.3 × 10^{-7}(0.9 × 10^{-7}) Ω^{-1} cm^{-1} was calculated from 20 measurements.

Similar to neutral phenyl viologen, **1** and **2** are good electrical conductors for even-electron, undoped molecules; typical undoped, even-electron conjugated molecules have single-crystal conductivities in the range from 10^{-15} to 10^{-18} Ω^{-1} cm^{-1}.[34] The conductivity of **1** is about an order of magnitude smaller than that of neutral phenyl viologen,[1] and it is not surprising that the presence of insulating octyl groups in **1** decreases its conductivity relative to the parent neutral phenyl viologen. The conductivity of **2** is about 20 times higher than that of **1**. To compare the conductivity of **1** and **2**, their solid-state structures must be considered. Powder X-ray diffraction indicates that **1** packs in a layered structure in the solid state, similar to 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl (see below). The solid-state structure of **2** can also be considered layered, with the layers stacking along the *a* crystallographic direction and the molecules of **2** within those layers being very tilted with respect to *a*. Electrical conductivity in **2** would occur mainly within the *b*−*c* plane. Although the intermolecular contacts between molecules of **2**

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(33) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(34) Gutmann, F.; Lyons, L. E. *Organic Semiconductors*; John Wiley & Sons: New York, 1967.

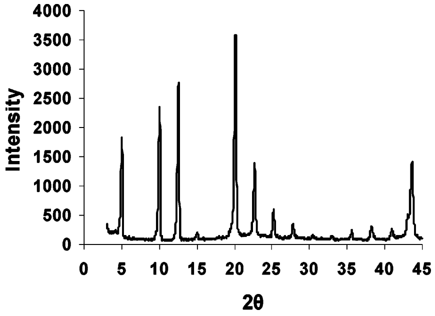

Figure 8. Powder X-ray diffraction pattern of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl; $\lambda = 1.542$ Å.

in its layers and those between molecules of **1** in its layers are different, and a comparison between the conductivity of the two must be made with that fact in mind, the 20-fold higher conductivity of **2** does seem to imply that hole transfer between molecules of **2** in the solid state is particularly facile.

Solid-State Structure and Properties of 4,4′′′′-Di-*n*-octyl-*p*-quaterphenyl. The molecule 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl has not been reported before. In fact, except for isolated reports of the methyl[35] and *n*-hexyl derivatives,[36] no 4,4′′′′-di-*n*-alkyl-*p*-quaterphenyls have been investigated. In contrast, the similar α,*ω*-di-*n*-alkylsexithiophenes and α,*ω*-di-*n*-alkylquaterthiophenes have been thoroughly examined as the active components of thin-film transistors.[5] The unfunctionalized parent compound *p*-quaterphenyl does function in thin-film transistors,[37] so it seems that studies of 4,4′′′′-di-*n*-alkyl-*p*-quaterphenyls in thin-film transistors may be fruitful, and we have shown in this paper that they are very easily synthetically accessible. Furthermore, as shown below, 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl is arranged in the solid state in the layered structure of most materials currently in use in organic thin-film transistors.

Powder X-ray diffraction of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl (Figure 8) shows strong diffraction peaks at 2θ intervals of about 2.5°, with some absences. The diffraction pattern indicates a layered structure with a layer thickness of 35.5 Å. Crystals of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl are thin plates and the layers are presumably parallel to the two long dimensions of the plates. When the diffraction experiment is performed, the plates are preferentially lying flat on the sample holder, so only diffraction peaks due to the interlayer spacings are observed. A layer thickness of 35.5 Å is consistent with 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl molecules packed in two-dimensional sheets. A set of four molecules in a configuration of minimal energy determined by molecular mechanics (in Chem3D) is shown in Figure 9, which can be viewed as a part of one sheet of thickness 36.6 Å, in reasonable agreement with the X-ray diffraction data. The related molecules α,*ω*-dihexylquaterthiophene[4] and α,*ω*-dihexylsexithiophene[3] have similar solid-state structures.

Figure 10 shows the differential scanning calorimetry (DSC) curves of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl. Runs from 25 to 260 °C and back to 25 °C were performed three times sequentially, and the results from each run were similar. Data from the third run is shown. The molecule is in a crystalline state at room temperature and then undergoes transitions to two different liquid crystalline mesophases at 81 °C and 99 °C. Melting occurs at 284 °C, so there is a very broad temperature range over which 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl exists as a liquid crystal. The related molecule α,*ω*-dihexylquaterthiophene undergoes a similar transition at 84 °C and melts at 179 °C.[4]

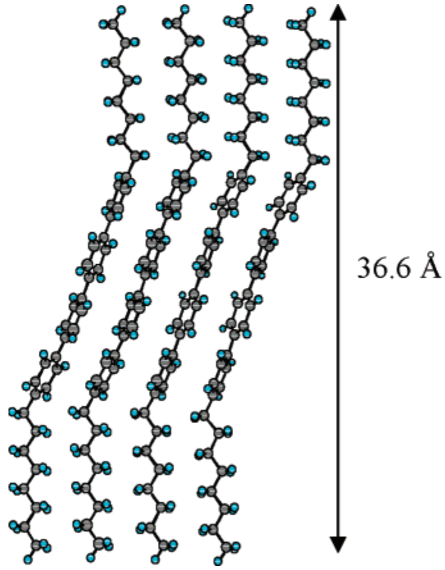

Figure 9. Set of four molecules of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl in an energy-minimized configuration, indicating a layer thickness of approximately 36.6 Å.

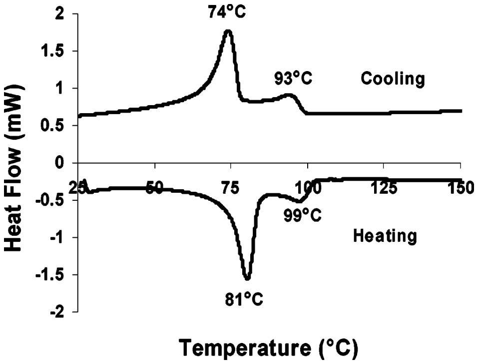

Figure 10. DSC curves for 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl in both the heating and cooling directions. Data from the third of three cycles is shown.

Cocrystallization of 1 and 2 with 4,4′′′′-Di-*n*-octyl-*p*-quaterphenyl. Both **1** and **2** were originally intended to be dopants for 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl, so their cocrystallization with 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl was investigated. Slow cooling a hot solution of a 9:1 mixture 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl and **1** in toluene results in pale red plate-shaped crystals, while a similar crystallization of 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl and **2** results in blue-green plate-shaped crystals. Inspection of both materials under an optical microscope revealed that all the crystals were the same color and each was uniform in color, implying a random distribution of the dopant molecules within the host. Treatment of a sample of each set of cocrystals with ferrocenium hexafluorophosphate in pyridine-d_5 and integration of the ^{1}H NMR (obtained at 95 °C) resonances of $\mathbf{1}^{2+}$ or $\mathbf{2}^{2+}$ versus 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl indicated doping levels of 11% and 10% for **1** and **2**, respectively. Powder X-ray diffraction of sets of cocrystals was very similar to that of pure 4,4′′′′-di-*n*-octyl-*p*-quaterphenyl, showing that the layered structure of the host was maintained in the cocrystals.

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(35) Gilman, H.; Weipert, E. A. *J. Am. Chem. Soc.* **1957**, *79*, 2281−2283.
(36) Kovyrzina, K. A.; Tsvetkova, T. A. *Zh. Org. Khim.* **1977**, *13*, 2395−2398.
(37) Gundlach, D. J.; Lin, Y. Y.; Jackson, T. N.; Schlom, D. G. *Appl. Phys. Lett.* **1997**, *71*, 3853−3855.

There was an additional broad peak in the powder diffraction pattern of both sets of cocrystals at $2\theta = 26.4°$, corresponding to a spacing of 3.37 Å. The origin of this extra peak is unknown, although it is close to interplanar spacing in an aromatic π-stacked material. Although substitutional cocrystallization of both dopants with the host was successful, neither doped material displayed any electrical conductivity, as would be expected from the solution-phase electrochemical potentials.

Conclusions

The new molecule 4,4‴-di-*n*-octyl-*p*-quaterphenyl was synthesized by a straightforward one-step procedure, and it is representative of an unexplored class of molecules, the di-*n*-alkyl-*p*-quaterphenyls, that may find use as the active components of organic thin-film transistors. It is a liquid crystal over a wide temperature range, from about 81 °C to its melting point at 284 °C. The isostructural molecule **2** is a neutral “extended viologen” and is the first neutral extended viologen to be isolated. Our aim in synthesizing **2** was to create a molecule that is a stronger reducing agent than its isomer **1**, and indeed **2** is, to the best of our knowledge, the most reducing neutral organic molecule that has been isolated. The electronic structure of **2** is somewhat enigmatic, although it is clear that a diradical form, either singlet or triplet, makes an important contribution to the electronic structure. The electronic structure of **2** appears to be closely related to that of the classic molecule Chichibabin’s hydrocarbon.

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Supporting Information Available: Synthetic, spectroscopic, and other experimental details, ^{1}H NMR of **2**, crystal data for **2** (and a separate CIF file), current−voltage plots for **2**, image of the HOMO of **2**, and a complete version of ref 25 are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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