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Oxidation of Tetraphenylhexaazaanthracene: Accessing a Scissor Dimer of a 16π Biscyanine

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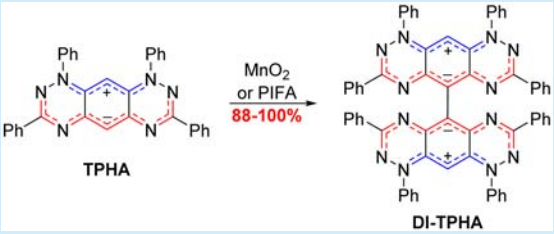
Ⓢ *Supporting Information*

ABSTRACT: Tetraphenylhexaazaanthracene (**TPHA**), a fluorescent zwitterionic biscyanine with a closed-shell singlet ground state, on treatment with manganese dioxide or phenyliodine bis(trifluoroacetate) (**PIFA**), undergoes oxidative dimerization to give a near-zero dipole scissor 5,5′-dimer **DI-TPHA**. Both acene components of the new dimer **DI-TPHA** maintain their biscyanine closed-shell singlet ground state motifs, as judged by analysis of both single crystal X-ray crystallographic and density functional theory computational studies; however, unlike **TPHA**, **DI-TPHA** is only very weakly fluorescent.



Acenes with zwitterionic biscyanine motifs are unusual, as their central arenes have lost their aromaticity by parting their π electrons. The first example, 5,7-diphenyl-5*H*,12*H*-quinoxalino[2,3-*b*]phenazine (**DPTAP**, a.k.a. diphenylisofluorindine) was reported as early as 1896, but at that time the exact electronic nature of the compound was unclear.[1] While these compounds were of interest as potential textile dyes,[2] little more was reported until 1998 when Wudl prepared the zwitterionic biscyanine of tetraphenylhexaazaanthracene **TPHA**[3] (Figure 1).

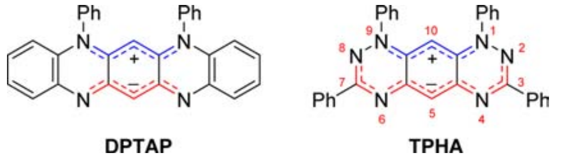


Figure 1. Structures of **DPTAP** and **TPHA** with IUPAC numbering.

Since then, there has been increased interest in their potential use as organic field effect transistors (OFETs),[4] as well as other applications such as organic light-emitting diodes (OLEDs), memory devices, phototransistors, solar cells, photoelectrical chemical cells, sensors, and conductors.[5]

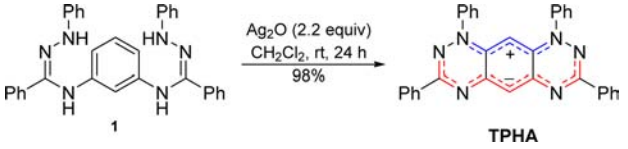
Several recent developments include the improved synthesis of **TPHA**[6] and **DPTAPs**,[7] the synthesis of heptaazaanthracenes,[8] hexa-[9] and octaazapentacene[10] analogues, the synthesis of asymmetric acene systems,[11] and Oakley's sulfur and selenium containing systems.[12]

Computational studies on biscyanine acenes to predict the energy differences between the triplet and singlet ground states,[13] optical studies,[7a,8,9a] and liquid crystalline[14] and molecular monolayer[15] behavior have been reported.

Surprisingly, further synthetic chemistry is limited to N-protonation[7a,8b,9a] or alkylation[7b,11a,12b−j,16] of the nitrogens on the −ve cyanines and also to the oxidation of **DPTAP** to afford *para*-quinonimine systems[16a] and finally the reductive ring contraction of **TPHA** to afford imidazolo-fused systems.[17]

Recently, we reinvestigated the synthesis of **TPHA**, which involved the oxidation of the bisamidrazone **1** and identified Ag_2O as a superior oxidant that gave **TPHA** in near-quantitative yield (Scheme 1).[6]

Scheme 1. Improved Route to TPHA



During screening of oxidants for the conversion of the bisamidrazone **1** to **TPHA**, we discovered that MnO_2 (10 equiv) in CH_2Cl_2 at ca. 20 °C gave after 24 h in addition to the desired **TPHA** (74%) a low yield (2%) of the dedihydro 5,5′-dimer of **TPHA** namely 1,1′,3,3′,7,7′,9,9′-octaphenyl-1*H*,1′*H*-[5,5′-bibenzo[1,2-*e*:5,4-*e*′]bis([1,2,4]triazine)]-9,9′-diium-6,6′-diide (**DI-TPHA**). This new dark purple compound was more polar than **TPHA** [R_f 0.25 (**DI-TPHA**) vs 0.44 (**TPHA**) in *n*-hexane/Et_2O 50:50 on silica TLC], was nonfluorescent, showed sharp line NMR spectra indicating a closed-shell electronic ground state, and was thermally stable: it did not melt up to 400 °C, but differential scanning calorimetry (DSC) revealed a decomposition onset at 415.9 °C; see Sect. S7 and S8 in the Supporting Information (SI).

The structure of **DI-TPHA** was derived from an analysis of the spectroscopic data (Sect. S1 in the SI) and further

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supported by X-ray diffraction studies (CCDC-1446791). Single crystals of **DI-TPHA** were obtained from slow cooling of a concentrated solution in toluene. Molecules of **DI-TPHA** crystallize in the monoclinic space group $P2_1/n$, with one **DI-TPHA** molecule in the asymmetric unit ($Z = 4$) (Figure 2).

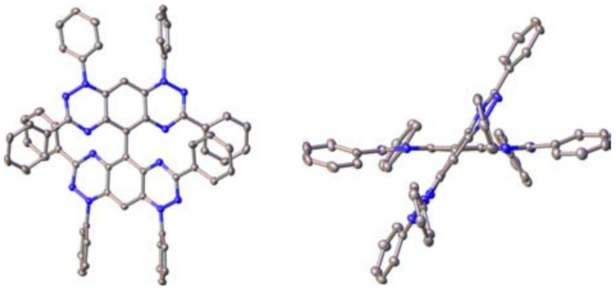


Figure 2. Crystal structure of **DI-TPHA** (hydrogen atoms omitted for clarity) (CCDC-1446791).

The two azaacene subunits are connected via a long single C−C bond [1.491(2) Å] and adopt a scissor geometry with a torsion angle of 58.3(2)°. The C-phenyls of **DI-TPHA**, in comparison to **TPHA**, deviate from the acene plane by ca. 20°, while one pair of *N*-phenyls are twisted in a disrotatory manner with torsion angles of 55.5(2)° and 61.8(2)° and the other pair twisted in a conrotatory manner with torsion angles of 53.5(2)° and 55.8(2)°. Tentatively, we attributed these differences to packing effects.

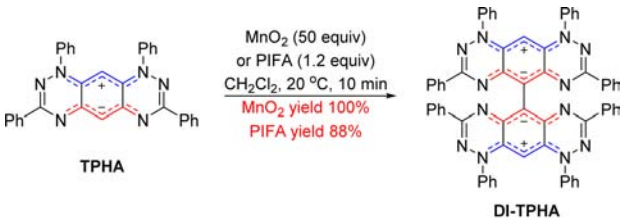
The corresponding bond lengths in both azaacene subunits of **DI-TPHA** are similar to those of **TPHA** (Table S1 in the SI), which strongly supports the presence of a zwitterionic ground state: both +ve and −ve cyanines indicate bond equalization, and the oppositely charged cyanines are typically connected by long C−C bonds (ca. 1.45 Å): these carbons lie at nodal points leading to increased σ character and longer bonds.

The crystal packing of **DI-TPHA** (Sect. S4 in the SI) showed molecules related by three symmentry elements. The phenyl groups on both acene subunits participate in edge-to-edge, edge-to-face, and face-to-face intermolecular contacts leading to tight crystal packing with few voids, which may explain the compound's high thermal stability.

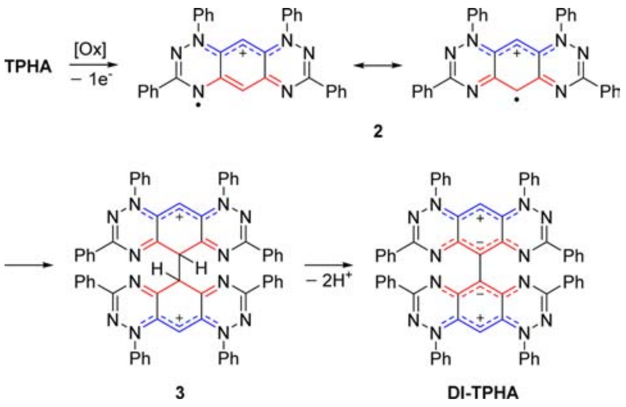
After a brief investigation of the reaction conditions (Sect. S2 in the SI), **DI-TPHA** was prepared in high yield by treating pure **TPHA** with either excess MnO_2 (50 equiv) or phenyliodine bis(trifluoroacetate) (PIFA)[18] (1.2 equiv) in CH_2Cl_2 at ca. 20 °C for 10 min (Scheme 2); despite the need for excess oxidant the MnO_2 was superior, as it avoided the need for chromatography.

Mechanistically, the oxidative dimerization of **TPHA** can be rationalized by considering the abstraction of one electron from the electron-rich negative 10π cyanine of **TPHA** to give a resonance stabilized cation radical **2**. This can then dimerize at C-5 to give the dication **3** that on proton loss releases the observed **DI-TPHA** (Scheme 3). While to the best of our knowledge this coupling is new within the zwitterionic biscyanine class of acenes, oxidative C−C dimerizations of structurally related enamines and metalated hydrazones are known.[19]

Scheme 2. Conversion of TPHA to DI-TPHA



Scheme 3. Proposed Oxidative Dimerization of TPHA



Further comparisons between **DI-TPHA** and **TPHA** included cyclic voltammetry, electronic spectroscopy, and density functional theory (DFT) computational studies. The UB3LYP/6-311G(2d) computational method previously[6] used for **TPHA** was not used on **DI-TPHA** owing to limitations with our computer infrastructure. Comparisons of **TPHA** and **DI-TPHA** were carried out at the UB3LYP/6-31G(d) level of theory (see Table S3 in the SI for related **TPHA** data).

DI-TPHA exhibits three oxidations ($E_{1/2}{}^{0/+1}$ 0.57 V, $E_{1/2}{}^{+1/+2}$ 0.73 V, and $E_{1/2}{}^{+2/+3}$ 1.26 V vs Ag/AgCl) and one reduction ($E_{1/2}{}^{-1/0}$ −1.39 V vs Ag/AgCl) (Figure 3). After 10 cycles (100 mV·s^{-1}) only the third oxidation ($E_{1/2}{}^{+2/+3}$ vs Ag/AgCl) remained electrochemically stable, while the reduction was only partially electrochemically stable. For comparative purposes the electrochemical behavior of **TPHA** exhibited two reversible reductions ($E_{1/2}{}^{-1/0}$ −1.27 V and $E_{1/2}{}^{-2/-1}$ −1.53 V vs Ag/

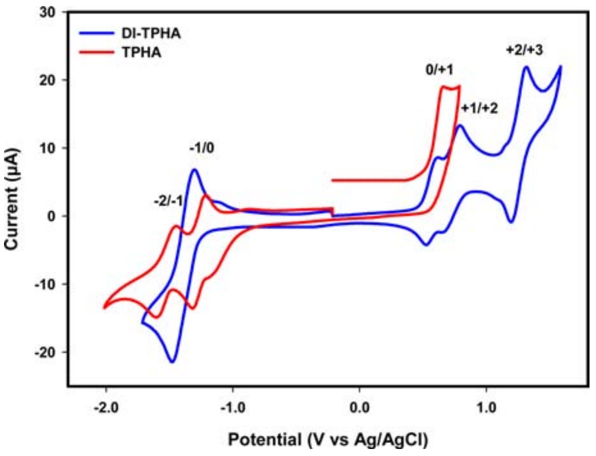


Figure 3. Cyclic voltammogram for **TPHA** (red) and **DI-TPHA** (blue) in CH_2Cl_2 (1 mM), *n*-Bu_4NBF_4 (0.1 M) as an electrolyte. Pt disk and Pt wire were used as working and counter electrodes, respectively, and Ag/AgCl as reference electrode. Scan rate 100 mV·s^{-1}, temp 20 °C, internal reference: Fc/Fc$^+$ (0.352 V).

AgCl), of which only the first was electrochemically stable after 1 cycle at 100 mV·s^{-1}, and an electrochemically unstable irreversible oxidation ($E_{1/2}{}^{0/+1}$ = 0.64 V vs Ag/AgCl) (Figure 3) (Sect. S6 in the SI). Our cyclic voltammetry data for **TPHA** matched those reported by Wudl et al.[3a]

DI-TPHA also exhibited similar optical properties to **TPHA**, suggesting minimal excitonic coupling of the two biscyanines. Unlike **TPHA** (μ_1 6.48 D), **DI-TPHA** (μ_1 0.11 D) showed no negative solvatochromism which was attributed to the opposing dipoles of the zwitterionic azaacene subunits in **DI-TPHA** which cancel out (Figure S9 in the SI). Furthermore, the absorption spectrum of **DI-TPHA** was broader than that of **TPHA** with a "0−0" vibronic transition at 600 nm, red-shifted by 11 nm with respect to the **TPHA** band; however, the rest of the spectrum overlapped that of **TPHA** with almost identical vibronic band intensities (Figure 4).

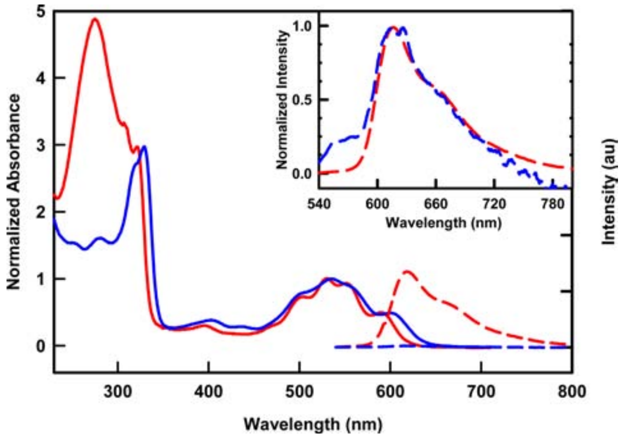


Figure 4. Absorption (solid line) and emission (dashed line) spectra of **TPHA** (red) (1.32 × 10^{-6} mol L^{-1}) and **DI-TPHA** (blue) (6.97 × 10^{-7} mol L^{-1}) in MeCN: absorbance normalized with respect to the 530 nm low energy band; excitation wavelength for the emission spectra is 530 nm. Inset: the respective normalized emission spectra.

Tentatively, electron density delocalization between the two biscyanines in the orbitals involved in the lowest energy transition accounted for the red shift. DFT computational studies indicated the changes in the orbital electron densities involved in the higher energy transitions mimicked those observed in **TPHA**,[6] which explained the similarity of the absorption spectra. Nevertheless, the TD-DFT computed vertical excitations of **DI-TPHA** (Table S2 and Figure S7 in the SI) differed from those of **TPHA**, in that they were of mixed character; furthermore, the visible absorption bands of **DI-TPHA** consisted of at least two different transitions.

The fluorescence spectra of **DI-TPHA** and **TPHA** were essentially identical (Figure 4, inset); however, the emission quantum yield in **DI-TPHA** was significantly diminished. Examination of the calculated energy levels of the dimer (Figures S4, S5, and S7 in the SI) revealed that the lowest energy optically allowed transition possessed charge transfer character[20] which tentatively explained the significant reduction in the emission quantum yield.

Geometry optimizations of both the singlet and triplet ground states of **DI-TPHA** at the DFT UB3LYP/6-31G(d) level of theory revealed interesting features. First, the zwitterionic biscyanine singlet state was the energetically more favorable ground state (ΔE_{ST} −0.65 eV) and only marginally less favorable than that of **TPHA** (ΔE_{ST} −0.68 eV). This agreed with the marginally smaller $\Delta E_{\mathrm{HOMO-LUMO}}$ gap of 2.15 eV (Figure S4 in the SI) vs 2.23 eV for **TPHA**. The low ΔE_{ST} values indicated that **DI-TPHA** can potentially undergo singlet fission.[21]

Furthermore, the singlet ground state geometry adopts a cruciform motif with a torsion angle of 86.83° while the triplet state geometry adopts an open scissor motif with a torsion angle of 78.31° (Figure S8 in the SI). Reductions in torsion angle can enable more efficient orbital overlap and π delocalization that can favor the triplet state.[22] Nevertheless, while the X-ray data (Figure 2) gave a scissor geometry, a bond length comparison of the computed and crystallographic data supported the charge separated zwitterionic biscyanine structure (Table S1 in the SI). Presumably, the presence of a scissor motif in the X-ray structure is due to packing and not electronic effects.

Further support for the singlet state comes from the electrostatic potential map of **DI-TPHA** that shows significant negative electron density on either side of the C−C bond that joins the two hexaazaanthracenes (Figure 5).

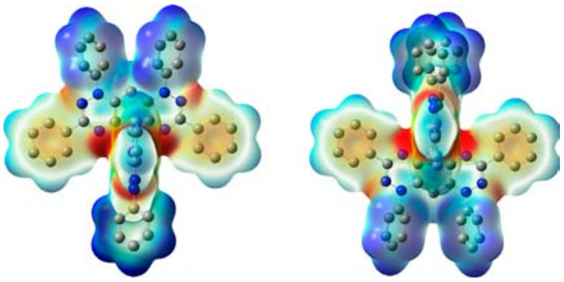


Figure 5. Calculated electrostatic potential map of **DI-TPHA** [UB3LYP/6-31G(d) level of theory]; red = −ve electron density, blue = +ve electron density. Right and left diagrams correspond to orthogonal viewing angles.

In conclusion, **TPHA** has been oxidatively dimerized to afford a 5,5′-dimer **DI-TPHA** which adopts a scissor motif in the solid state and maintains the singlet ground state biscyanine motif of the starting **TPHA**. Overall, **TPHA** and **DI-TPHA** display similar optical [$E_g{}^{\mathrm{opt}}$ 1.99 eV (**TPHA**) vs 1.93 eV (**DI-TPHA**)] and electrochemical [$E_g{}^{\mathrm{echem}}$ 1.91 V (**TPHA**) vs 1.96 V (**DI-TPHA**) band gaps (Table S4 in the SI). This was not surprising considering the orientation of the two azaacene subunits of **DI-TPHA** that are essentially noninteracting. Nevertheless, the dimer conformation in **DI-TPHA** enabled a charge transfer in the first excited state that diminished the dimer's fluorescence. Further studies on this and related dimers are underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00222.

Experimental, computational, and spectroscopic characterization data (PDF)

Crystallographic file for **DI-TPHA** (CIF)

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Notes

The authors declare no competing financial interest.

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