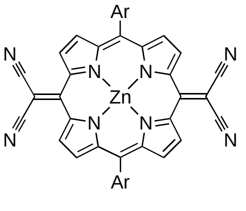
Synthesis and Crystal Structure of a Cumulenic Quinoidal Porphyrin Dimer with Strong Electronic Absorption in the Infrared**

Iain M. Blake, Leigh H. Rees, Tim D. W. Claridge, and Harry L. Anderson*

The remarkable optoelectronic and nonlinear-optical behavior of *meso*-alkyne-linked porphyrin oligomers can be attributed to the contribution of cumulenic quinoidal mesomeric forms, particularly in the excited states.[1] Recently we reported the synthesis of the quinoidal 5,15-dialkylideneporphyrin **1**, from dibromoporphyrin **2**, as a first step towards the preparation of fully quinoidal porphyrin oligomers.[2] The $C(CN)_2$ end groups stabilize this quinoidal structure, just as they stabilize 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[3] We have now extended this approach to gain access to a cumulenic quinoidal porphyrin dimer **3** (see Scheme 1). The phenomenal conjugation in this compound results in amazingly intense and red-shifted electronic absorption ($\lambda_{max} = 1080$ nm, $\varepsilon = 1 \times 10^5\,\text{M}^{-1}\text{cm}^{-1}$).



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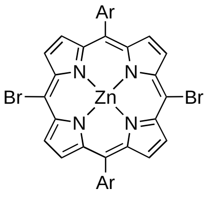

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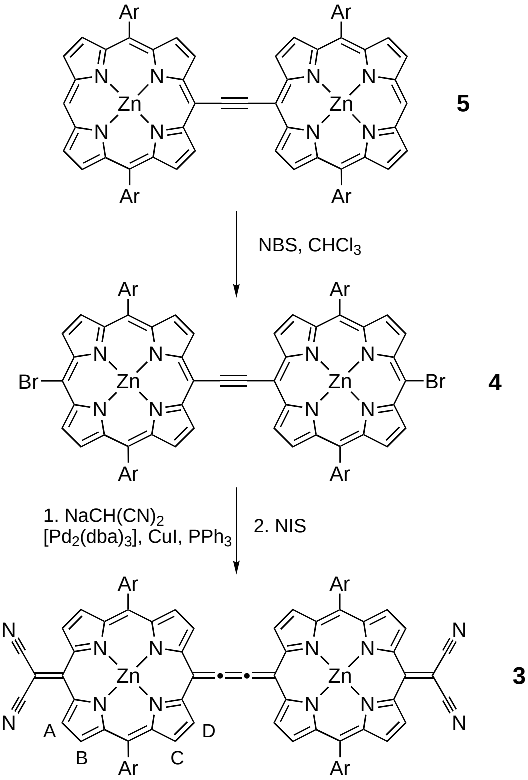
The cumulenic porphyrin dimer **3** was prepared from dibromoporphyrin dimer **4**, as summarized in Scheme 1. After exploring several routes to **4**, we were surprized to discover that it is formed in near-quantitative yield by direct bromination of **5** (prepared using the route of Therien et al.)[1b] with *N*-bromosuccinimide (NBS) in chloroform at 0 °C.[4] Bromination occurs exclusively at the two free *meso* positions, with no competing substitution at the β-pyrrolic positions or addition to the alkyne. Dibromo dimer **4** was converted into **3** in 34% yield by palladium/copper catalyzed Takahashi coupling[2, 5] with the malononitrile anion followed by oxidation with *N*-iodosuccinimide (NIS).[6] This sequence is similar to the reaction used to prepare **1** from **2**, except in that case no oxidant was required as the intermediate spontaneously oxidized in air, whereas the synthesis of **3** requires NIS.



Scheme 1. Synthesis of **3**. dba = dibenzylideneacetone.

The ^1H and ^{13}C NMR spectra of **3** were assigned using a combination of NOESY, HMQC, and HMBC experiments. Crucially, a HSQC-NOESY experiment[7] was used to observe an NOE between the equivalent H_D protons across the symmetry plane at the center of the molecule (by observing an NOE between H_D and the ^{13}C satellites of this same resonance),[8] which allowed the pairs H_A/H_D and H_B/H_C to be unambiguously distinguished (Scheme 1). Part of the ^1H NMR spectra of **4** and **3** are compared in Figure 1a, b; all the β-pyrrolic resonances are shifted up-field in **3** because of the absence of an aromatic porphyrin ring current, as observed previously in **1**.[2] The crystal structure[9] of $\mathbf{3}\cdot 2\,C_5H_5N$, illustrated in Figure 2, shows that the 62-atom chromophore adopts a bow-shaped geometry in the solid state, with both pyridine molecules coordinated to the concave surface. The bond lengths in each macrocycle are similar to those in $\mathbf{1}\cdot C_5H_5N$ and the bond lengths in the central cumulene unit (marked on Figure 2b) are typical for a cumulene.[10]

Success in preparing the cumulenic dimer **3** encouraged us to attempt the synthesis of a shorter quinoidal porphyrin dimer **6** (conceptually derived from **3** by deletion of the two central carbon atoms). At first sight, **6** might appear to be an unrealistic synthetic target since the clash between the inner β-pyrrolic protons could make it difficult to form the central *meso*–*meso* double bond, but strained alkenes of this type[11] have been prepared, such as 29,29,30,30-tetracyanobianthraquinodimethane (TBAQ).[12] We found that the *meso*–*meso* linked dibromo dimer **7** (prepared by oxidative coupling of

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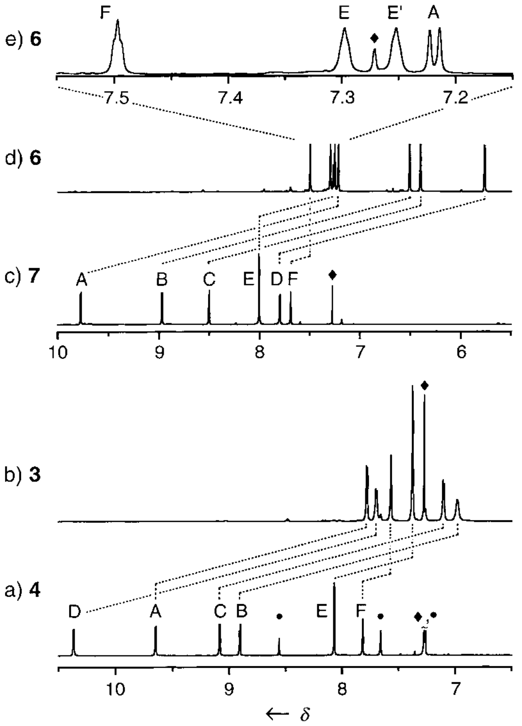


Figure 1. NMR spectra of a) **4**, b) **3**, c) **7**, and d, e) **6** in $C_5D_5N/CDCl_3$ (◆ and ● indicate $CHCl_3$ and C_5D_4HN, respectively).

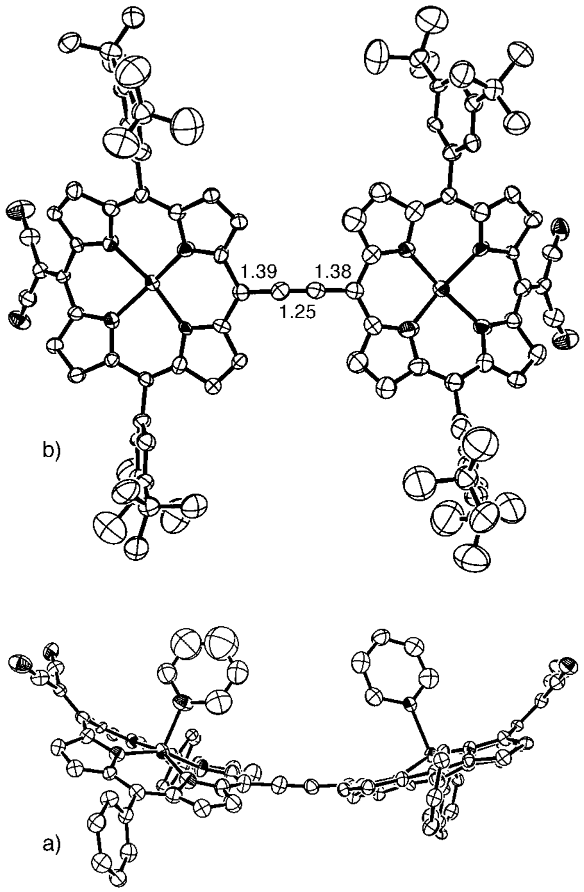
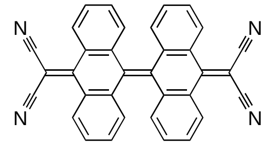
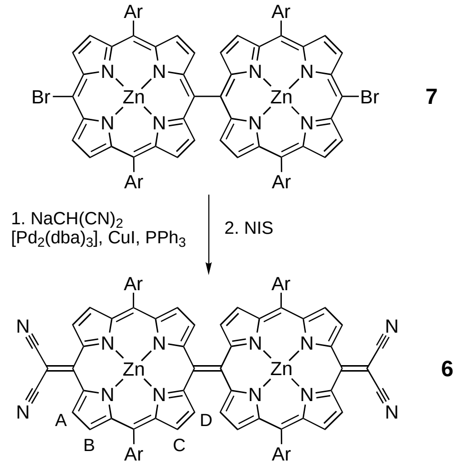


Figure 2. Structure of $\mathbf{3}\cdot 2\,C_5H_5N$ in the solid state, with 40% probability ellipsoids: a) side view (omitting *t*Bu groups) and b) plan view (omitting pyridine ligands) showing the bond lengths [Å] in the central cumulene unit; the estimated standard deviation in these bond lengths is 0.03 Å.

the monobromoporphyrin as reported by Osuka and co-workers)[13] could be converted into **6** in 36% yield (Scheme 2) using identical reaction conditions to those used to prepare **3** from **4**. The ^1H NMR spectrum of **6** (Figure 1d, e) is shifted up-field relative to **7**, similar to that of **3** relative to **4**.[14] Further evidence for the quinoidal nature of **6** comes from the observation of a ^{13}C signal at $\delta = 72.6$ in the ^{13}C NMR spectrum corresponding to the central carbon atom of the $C(CN)_2$ unit; this resonance occurs at $\delta = 76.5$ and 73.5 in **1** and **3**, respectively. Whereas the ^1H and ^{13}C NMR spectra of **3** are consistent with a time-averaged planar D_{2h} geometry, those of **6** show the molecule is nonplanar, as anticipated from the clash between the inner β-pyrrolic protons: the resonances of the aryl protons *ortho* to the porphyrin (E, E') and the *tert*-butyl protons are both split into two signals of equal intensity (Figure 1e). Corresponding splittings are also observed by ^{13}C NMR spectroscopy. The C_{2h} and D_2 nonplanar geometries shown in Figure 3 are both consistent with these NMR spectra. Molecular mechanics calculations[15] indicate that the D_2 geometry is more stable by 105 kJ mol^{-1}; these calculations correctly predict that the C_{2h} geometry of TBAQ is preferred,[12] although in this case the C_{2h}/D_2 energy difference is only 23 kJ mol^{-1}.

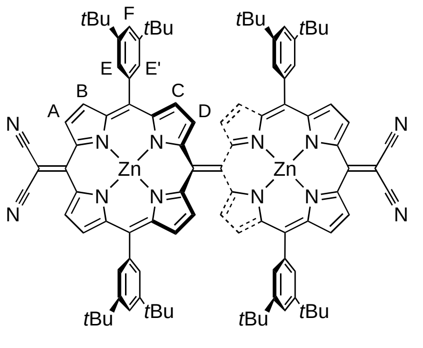


TBAQ

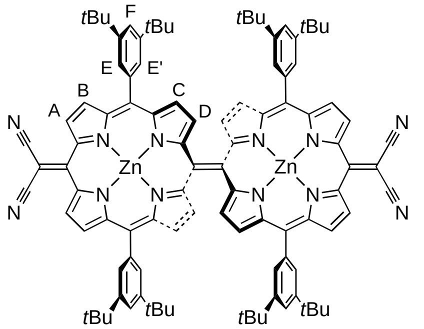


Scheme 2. Synthesis of **6**.

The electronic absorption spectra of **1**, **3**, and **6** are compared with those of **2**, **4**, and **7** in Figure 4, and illustrate the amazing increase in conjugation accompanying quinoidalization. The less bathochromic absorption of **6** (compared to **3**) is probably a consequence of its nonplanarity, which must reduce the π overlap. The efficient conjugation in **3** shifts its optoelectronic activity into a region where few chromophores operate. The absorption spectrum of **3** resembles those of the electrogenerated porphyrin dimer dianions of Arnold, Heath,



folded C_{2h} conformer



twisted D_2 conformer

Figure 3. The C_{2h} and D_2 conformers of **6** are both consistent with its NMR spectra.

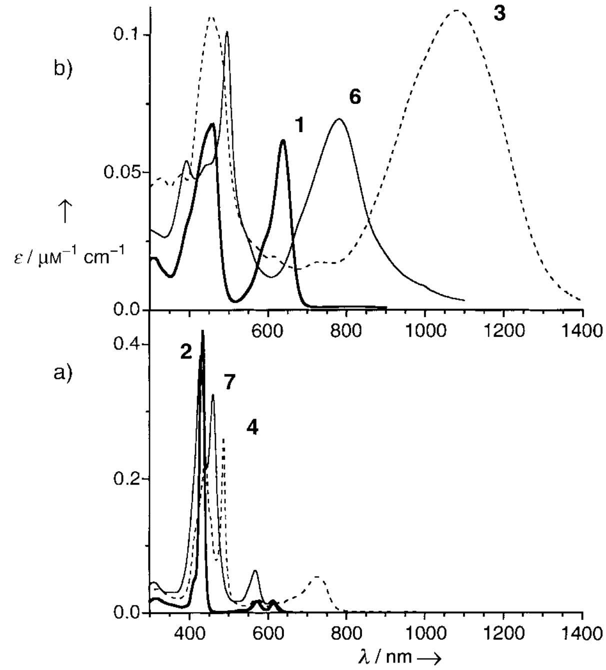


Figure 4. Absorption spectra of a) dibromoporphyrins **2** (bold), **4** (dashed), and **7** (plain) and b) quinoidal compounds **1** (bold), **3** (dashed) and **6** (plain) in 1% C_5H_5N/CH_2Cl_2.

and James,[1c] which also have strong bands around 1000 nm, yet **3** is a stable neutral compound. This near-infrared region is important because of the widespread use of neodymium yttrium aluminium garnet (Nd-YAG) lasers, at 1064 nm, and because fibre-optic telecommunication systems operate in a nearby region (1300 nm). The optoelectronic and nonlinear optical properties of these new quinoidal porphyrin dimers are now under investigation.

Experimental Section

^{1}H and ^{13}C spectra were recorded in $C_5D_5N/CDCl_3$ at 500 MHz and 126 MHz respectively; UV/Vis spectra were recorded in 1% C_5H_5N/CH_2Cl_2.

4: NBS (26 mg, 0.14 mmol) was added to a solution of dimer **5** (105 mg, 0.069 mmol) in $CHCl_3$ (75 mL) and pyridine (0.75 mL) at 0°C. The mixture was stirred for 15 min then quenched with acetone (10 mL), evaporated and washed with methanol to yield the pure product as a black solid (100 mg, 86%).

3: Dibromo dimer **4** (40 mg, 0.024 mmol), $[Pd_2(dba)_3]$ (2.2 mg, 0.0024 mmol), PPh_3 (5.0 mg, 0.019 mmol), and CuI (1.8 mg, 0.0095 mmol) were dissolved in dry THF (25 mL) and pyridine (0.25 mL). Malononitrile (16 mg, 0.24 mmol) was added and the solution degassed before the addition of NaH (60% suspension in oil, 14 mg, 0.36 mmol). The mixture was heated to reflux under nitrogen for 15 h, then HOAc (20 μL, 0.36 mmol) was added and the volume reduced to 5 mL before being passed through a size exclusion column (1% cross-linked polystyrene/divinylbenzene SX1 Bio-Beads from Bio-Rad, 1% pyridine/toluene). The fractions containing the intermediate were evaporated and redissolved in $CDCl_3$ (600 μL) with C_5D_5N (10 μL) in a 5-mm NMR tube. NIS (6 mg, 0.03 mmol) was added and the cumulene was seen to form cleanly and instantly by ^{1}H NMR spectroscopy. The oxidized product was precipitated, after transfer from the NMR tube, by layered addition of methanol. The precipitate was washed with methanol to yield pure **3** as a black solid (14 mg, 34%). ^{1}H NMR: $\delta = 7.77$ (d, $J = 4.4$ Hz, 4H), 7.69 (d, $J = 4.4$ Hz, 4H), 7.56 (t, $J = 1.5$ Hz, 4H), 7.37 (d, $J = 1.5$ Hz, 8H), 7.10 (d, $J = 4.4$ Hz, 4H), 6.97 (br d, 4H), 1.39 (s, 72H); ^{13}C NMR: $\delta = 157.6$, 150.1, 149.8, 149.4, 147.5, 146.0, 138.5, 134.1, 131.7, 129.9, 129.2, 126.1, 125.2, 122.9, 122.7, 118.0, 112.0, 73.5, 35.0, 31.6; UV/Vis: λ_{max} ($\log \varepsilon$) = 455 (5.03), 1080 nm (5.04); MALDI-TOF-MS: m/z: 1650.9 [MH^+].

6: Dibromo dimer **7** (80 mg, 0.048 mmol) was converted into quinoidal dimer **6** (22 mg, 36% overall yield) using essentially the above procedure, except in this case the intermediate (51 mg, 65% yield) was crystallized from methanol prior to oxidation. ^{1}H NMR: $\delta = 7.50$ (t, $J = 1.7$ Hz, 4H), 7.30 (br d, 4H), 7.25 (br d, 4H), 7.22 (d, $J = 4.4$ Hz, 4H), 6.51 (d, $J = 4.4$ Hz, 4H), 6.40 (d, $J = 4.4$ Hz, 4H), 5.76 (d, $J = 4.4$, 4H), 1.39 (s, 36H), 1.32 (s, 36H); ^{13}C NMR: $\delta = 162.6$, 155.6, 150.2, 150.1, 150.0, 149.8, 147.0, 146.2, 137.8, 132.7, 132.1, 130.1, 125.7 (×2), 125.2, 123.1, 121.2, 117.3, 72.6, 35.3, 35.2, 31.9, 31.8; UV/Vis: λ_{max} ($\log \varepsilon$) = 392 (4.73), 494 (5.00), 780 nm (4.84); MALDI-TOF-MS: m/z: 1625.4 [MH^+].

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[8] NOESY and HSQC-NOESY experiments were carried out with a 300 ms mixing time at 294 K on a Bruker DRX500 instrument. All NOEs were negative.

[9] Crystals were grown by slow diffusion of *n*-pentane into a solution of $\mathbf{3}\cdot 2\,C_5H_5N$ in $CHCl_3$, over two weeks. Crystal data for $\mathbf{3}\cdot 2\,C_5H_5N\cdot 0.5\,C_5H_{12}\cdot 3\,H_2O$: $M_r = 1901.05$, monoclinic, space group *P*21/*c*, $a = 15.440(4)$, $b = 33.765(5)$, $c = 20.485(2)$ Å, $\beta = 94.64(2)°$, $V = 10644.5(33)$ Å^3, $Z = 4$, $T = 150(2)$ K, $\rho_{calcd} = 1.186\ g\,cm^{-3}$, $\mu = 0.508\ mm^{-1}$, blue/green prisms $0.30 \times 0.20 \times 0.15\ mm^3$, Enraf-Nonius DIP2000 image plate diffractometer, radiation $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å), ω scans, range $1.45 < \theta < 20$; measured reflections: 4436; independent reflections: 4436 ($R_{int} = 0.0000$), *R* values ($I < 2\sigma I$): $R1 = 0.1159$, $wR2 = 0.3212$, all data: $R1 = 0.1628$, $wR2 = 0.3711$. Structure refinement: full-matrix-block least-squares on F^2. max/min residual electron density $1.255/-0.393$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139644. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[14] No $^{12}C\text{-}H_D$ to $^{13}C\text{-}H_D$ NOE was observed in **6**, which is explained by the larger H_D–H_D distance in **6** (calculated: 2.9 Å for D_2 isomer; 2.6 Å for C_{2h} isomer) compared to that in **3** (crystallographic: 2.47 and 2.41 Å; calculated: 1.9 Å). The ^1H and ^{13}C NMR spectra of **6** were assigned by assuming that the most shielded β-pyrrolic proton is H_D.

[15] Molecular mechanics calculations were carried out using the CAChe 4.1 software from Oxford Molecular Ltd. with augmented MM2 parameters; MM3 gave similar results.

Fully Reversible Cyclic Dimerization of Diphosphanylketenimines Promoted by Intramolecular C–H···N Hydrogen Bonds[**]

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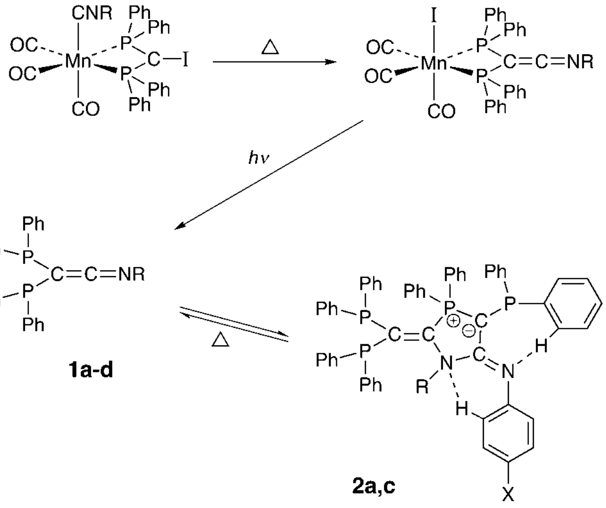
Ketenimines are important functional groups that show enhanced reactivity in nucleophilic addition and cycloaddition reactions. Furthermore, compounds containing this moiety are useful starting materials which have been applied in heterocycle chemistry.[1] We recently reported the synthesis of the diphosphanylketenimines $(PPh_2)_2C{=}C{=}NR$ (**1a**: R = Ph, **1b**: R = *t*Bu) by metal-assisted coupling of a transient diphosphanylcarbene with isocyanides (Scheme 1).[2] As these molecules combine the properties of diphosphanes with those of ketenimines, it was anticipated that new reactivity patterns could arise from them. Here we report a unique cyclic dimerization of *N*-aryldiphosphanylketenimines involving a new type of [2+3] cycloaddition reaction to give an azaphospha five-membered heterocycle featuring a phosphorus-ylide functionality. This dimerization is reversible under mild conditions and appears to be promoted by nonconventional CH···N hydrogen bonds.



Scheme 1. Metal-assisted synthesis of diphosphanylketenimines **1**. In the case of R = Ph or *p*-tolyl, reversible dimerization takes place to form **2**. **1a**: R = Ph; **1b**: R = *t*Bu; **1c**: R = *p*-tolyl; **1d**: R = xylyl; **2a**: R = Ph, X = H; **2c**: R = *p*-tolyl, X = Me.

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