A New Class of Cyanine-like Dyes with Large Bond-Length Alternation

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Polymethine cyanine dyes, which represent a class of charged chromophores with an odd number of π-conjugated carbons, have fascinated chemists for decades.[1−8] Cyanines display unique electronic and optical properties attributed to the strong electronic delocalization and the absence of any significant carbon−carbon bond-length alternation (BLA) along their backbones. The flatness of the corresponding electronic potential, illustrated in Figure 1, and the equivalence of their bond lengths make cyanine dyes the compounds to which simple free-electron theory can be applied in the most relevant way.[2,3,6] Recently, Thorley et al.[9] have reported the synthesis of carbocations consisting of two porphyrins linked by a π-conjugated bridge with an odd number of carbons and presenting alternating single and triple bonds. Interestingly, these cations were shown to possess linear and nonlinear optical properties analogous to those of cyanines.[9] Here, by using a joint theoretical and experimental approach, we demonstrate the correspondence between the polymethine cyanines and the new class of alkyne carbocations, in spite of their marked difference in BLA.

The degree of electronic delocalization and BLA along the backbone of π-conjugated molecules and polymers is widely regarded as a critical parameter determining their electronic, electrical, and optical properties.[10−12] In this context, cyanine dyes form a distinct class of compounds, as they present a nonalternated geometric structure; this key feature can be viewed as due to the interplay between the two valence-bond structures shown in Figure 1, which provides each bond with a length intermediate between those of single and double bonds. The vanishing BLA in cyanines is confirmed by several crystal structures.[13−16] The resulting fully delocalized electronic potential energy surface[17] depicted in Figure 1 imparts cyanines with a set of remarkable properties, including in particular the following:

(i) The lowest-energy optical bands are intense and very sharp, as the ground- and excited-state equilibrium geometries are (nearly) identical (see Figure 1, right).

(ii) Extrapolation of the optical gap in short cyanines would lead to a vanishing optical gap (metallic structure) in long chains, in accordance with the predictions of the simple free-electron model.[4−6] However, beyond some 13−15 carbon atoms, the symmetric structure of cyanines becomes unstable as the charge then localizes on one nitrogen atom; this results in the appearance in long cyanines of an asymmetric, strongly bond-alternated structure with an optical gap similar to those of regular polyenes.[18,19]

(iii) The molecular polarizabilities increase steeply with molecular length, L, in the way predicted by the free-electron model or Hückel theory:[20,21] the first-order (linear) static polarizability, α, evolves as $\sim L^3$, and the third-order static
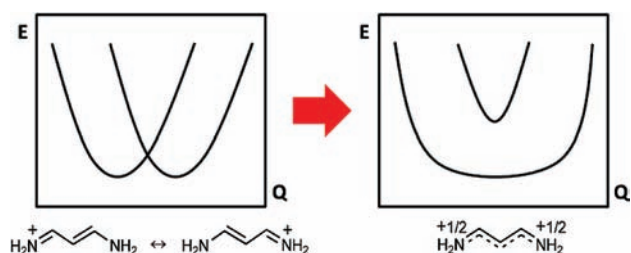
Figure 1. Illustration of the resonance forms and potential energy surfaces as a function of nuclear displacement (Q) for typical cyanine dyes. (left) Diabatic surfaces corresponding to the two individual resonance forms. (right) Resulting adiabatic surfaces of the ground and lowest excited states for the nonalternated structure.
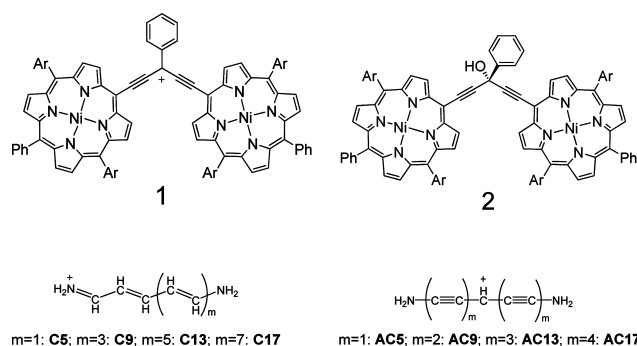
Figure 2. Chemical structures of the compounds considered here: Compounds **1** and **2**, model cyanines **C***n*, and model alkyne carbocations **AC***n*, where *n* represents the number of carbon atoms between the nitrogen atoms.

polarizability, γ, is negative (a characteristic of nonalternated structures) and evolves as $\sim L^{7−8}$. In contrast, α evolves as $\sim L^{1.5}$ and γ as $\sim L^{3−4}$ in polymethine dyes with BLA typical of polyene structures (BLA on the order of 0.1 Å).[22,23] In their unified theory of linear and nonlinear polarization, Marder et al.[12] have shown that zero-BLA structures (known in their work as the "cyanine limit", which can be considered to correspond to the "polymethine state" described by Dähne and Kulpe[4]) provide for the largest α and γ values at a fixed molecular length, as the transition dipoles between the ground and excited states are then maximized and the optical gap is minimized.

The synthesis and optical characterization of porphyrin dimers linked by an alkyne-based conjugated carbocation bridge with an odd number of carbons have been recently reported by Thorley et al.[9] These compounds include **1**, whose chemical structure is given in Figure 2. Intriguingly, in spite of the large BLA anticipated from the presence of the triple bonds, linear and nonlinear optical measurements indicate intense and sharp lowest-energy optical

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bands as well as very large and negative γ values in the near-IR (-2×10^{-31} esu at 1550 nm for **1**), in line with expectations one would formulate for zero-BLA cyanine dyes.[9]

In view of these results, our goal in this communication is to gain an understanding of the properties of these new alkyne carbocations and answer the question of whether these bond-alternated structures can be viewed as analogous to the class of (symmetric) polymethine cyanine dyes. As we show below, the features (i)−(iii) above, which are traditionally associated with cyanines, can be extended to the alkyne carbocations.

We used a joint theoretical and experimental approach combining first-principles Hartree−Fock and density functional theory (DFT) calculations and FTIR measurements to assess the geometric structures of the porphyrin dimer carbocation **1** and its alcohol precursor **2** (see Figure 2). Highly correlated intermediate neglect of differential overlap/multireference determinant configuration interaction (INDO/MRD-CI)[24,25] calculations were performed on model cyanines and alkyne carbocations (labeled **Cn** and **ACn**, respectively; see Figure 2 for chemical structures) to examine the evolution of the optical properties as a function of chain length. We note that in order to compare the properties of the two series of compounds on an equal footing, we only deal here with symmetric geometries.

The fully optimized geometry of **1** presents a strong BLA within the bridge; the single and triple bonds are calculated to have lengths of ~1.36 and ~1.21 Å, respectively, leading to a very large BLA degree of ~0.15 Å. These geometrical features can be understood from a simple analysis of the resonance forms that can be drawn for the **C5** and **AC5** compounds:

In **C5**: $^+$NH$_2$=CHCH=CHCH=CHNH$_2$ ↔ NH$_2$$^+$CHCH=CHCH=CHNH$_2$ ↔ NH$_2$CH=CH$^+$CHCH=CHNH$_2$ ↔ NH$_2$CH=CHCH=CH$^+$CHNH$_2$ ↔ NH$_2$CH=CHCH=CHCH=$^+$NH$_2$.

In **AC5**: $^+$NH$_2$=C=C=CHC≡CNH$_2$ ↔ NH$_2$$^+$C=C=CHC≡CNH$_2$ ↔ NH$_2$C≡C$^+$CHC≡CNH$_2$ ↔ NH$_2$C≡CCH=C=$^+$CNH$_2$ ↔ NH$_2$C≡CCH=C=C=$^+$NH$_2$.

On the basis of these resonance forms, the average bond orders can be evaluated; they are found to be the same in **C5** and **AC5** for the central bonds ($^7/_5$) but to differ by one full bond for the nominally triple bonds of **AC5** ($^{13}/_5$) compared with the same bonds in **C5** ($^8/_5$). It is also important to focus on the resonance forms in which the formal positive charge appears on a carbon; consideration of these underlines the fact that the alternation in π-electron density along the carbon backbone (see also Figure S1 in the Supporting Information), which is a hallmark of cyanine dyes (i.e., zero BLA and π-charge density alternation),[4,5] occurs in the same way in the **ACn** compounds.

FTIR spectra (FTS-7000, Varian) were acquired on ~2.7 mM solutions of **1** in chloroform/2% trifluoroacetic acid and **2** in chloroform. The 240 μm path length cuvette used for the measurements possessed KBr salt windows. Absolute absorbances of the solutions were obtained by referencing their spectra to the spectra of their respective solvents. Absolute integrated IR intensities were determined through a comparison with spectra of chloroform solutions of two reference compounds with known carbonyl mode intensities: acetone (190 km/mol) and ethyl acetate (320 km/mol).[26] All of the solvents were spectrophotometric grade (Sigma-Aldrich) and used as received. Figure 3 compares the FTIR spectra of **1** and **2** with DFT-calculated spectra (see the Supporting Information for details of the calculations). The carbocation spectrum is in general more intense (as expected from the presence of a net charge)[27] and presents a major new band at 2008 cm^{-1} and another at 2152 cm^{-1}. This IR region corresponds to vibrational modes in conjugated alkynes and substituted allenes (the latter appearing
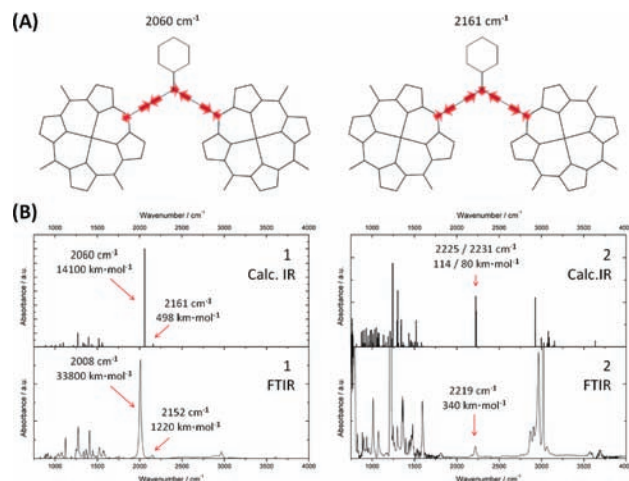

Figure 3. (A) Illustration of the normal modes of the DFT-calculated bands at 2060 and 2161 cm^{-1} for **1**. (B) Calculated IR (top) and experimental FTIR spectra in CHCl$_3$ (bottom) of **1** (left) and **2** (right). The signals at ~1750 and 2500−3500 cm^{-1} in the FTIR spectrum of **1** are residual peaks from trifluoroacetic acid.

because of the resonance forms of the molecule, as shown above). These bands are well-reproduced in the calculations (which were carried out on isolated molecules and gave bands at 2060 and 2161 cm^{-1}), as is the ratio of their intensities (27.6 exptl vs 28.3 calcd). The normal mode coordinates for the calculated bands at 2060 and 2161 cm^{-1} are illustrated in Figure 3; the origin of these modes is due mainly to antisymmetric and symmetric stretches, respectively, of the triple-like bonds. The very good agreement between theory and experiment confirms that compounds **1** and **ACn**, whose (fully optimized) calculated geometric structures can be simply viewed as averages over the sets of resonance structures, correspond to strongly bond-alternated structures.

The next step was to compare the optical properties of the cyanine dyes and alkyne carbocations as a function of the physical length, d, of the molecule (taken as the distance between the two nitrogen atoms in **Cn** and twice the distance between one of the nitrogen atoms and the central carbon atom in **ACn**). Here we relied on the highly correlated INDO-MRDCI technique coupled with the sum-over-states (SOS) perturbative approach,[28] a methodology which has been used successfully to describe the molecular polarizabilities of a wide range of conjugated compounds.[29−31] In the SOS framework, when a single excited state dominates the optical response, the static linear polarizability α is proportional to the square of the transition dipole moment between the ground and lowest excited state, M_{eg}, and inversely proportional to the transition energy, E_{eg}: $\alpha \approx M_{eg}^2/E_{eg}$. Figure 4 collects the calculated values of M_{eg}, E_{eg}, and α as a function of d for the **Cn** and **ACn** compounds. In all instances, E_{eg} and M_{eg} are seen to evolve linearly with d^{-1} and d, respectively, resulting in a cubic growth of α with d in both sets of compounds. (We recall that we considered here only rather short *symmetric* structures; for long chains, E_{eg} is not expected to extrapolate to zero,[19] as Figure 4 might imply).

A number of conclusions can be drawn from these results:

(i) The M_{eg} and E_{eg} values as a function of d indicate that the alkyne carbocations follow the same evolution predicted by simple free-electron theories, as do the symmetric cyanine dyes.

(ii) Remarkably, for similar molecular lengths, the α values in the **ACn** compounds are basically identical to (or even slightly larger than) those in their **Cn** counterparts.

(iii) Since the third-order polarizabilities γ are dominated by the negative SOS contribution ($\gamma \approx M_{eg}^4/E_{eg}^3$), γ is predicted
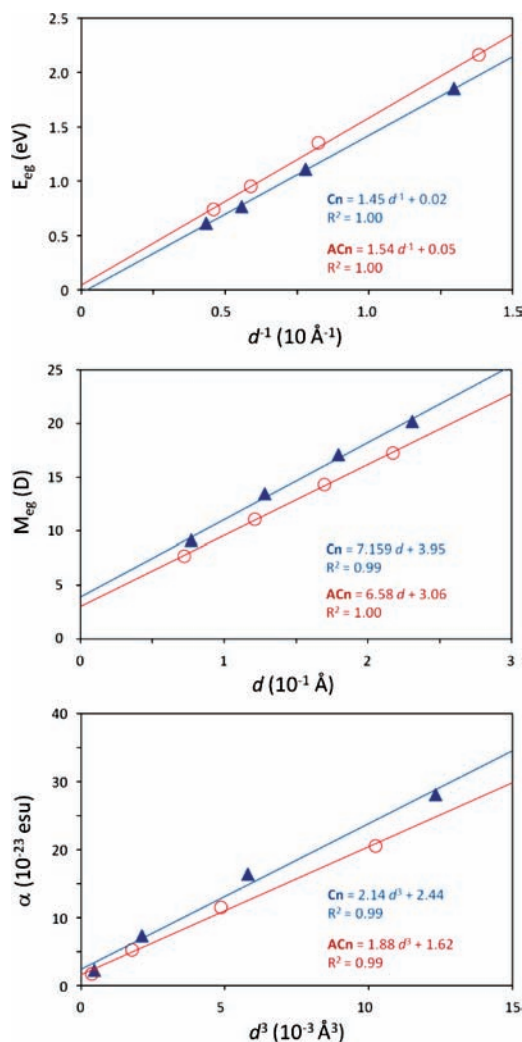
Figure 4. Evolution of the S_0-S_1 energy gap E_{eg}, S_0-S_1 transition dipole M_{eg}, and linear polarizability α as a functions of d^{-1}, d, and d^3, respectively, where d is the length of the π system (see the text for details) for the **Cn** (triangles) and **ACn** (circles) compounds.

to grow (in absolute values) in both series of compounds as d^7; again, this is in excellent agreement with free-electron theory as well as the results of correlated calculations on symmetric cyanine dyes performed by Pierce and co-workers.[20,21] Importantly, this evolution is fully consistent with the nonlinear optical characterization of compound **1**.[9]

The similarities between the **Cn** and **ACn** series can be rationalized by considering the bonding−antibonding patterns in the π molecular orbitals (see Figure S1 in the Supporting Information for a description of the frontier MOs of **C5** and **AC5**), which are essentially identical for each pair of corresponding MOs in the two compounds. Interestingly, except in the case of the fully bonding, most stable π MO, the π bonding remains weak between the carbons nominally bearing the triple bonds in **AC5** and between the corresponding carbons in **C5**. We suggest that this feature is a reason why the shortening of these bonds due to the perpendicular π system in **AC5** has only a weak impact on the electronic properties.

In conclusion, our theoretical results and the experimental data presented here and reported by Thorley et al.[9] unambiguously

establish that the *alkyne carbocations, in spite of their significant degree of bond-length alternation, behave in the same way as cyanine dyes*. They confirm that in these compounds (which could be considered as monomethine cyanine dyes such as Michler's hydro blue or Victoria green), the delocalized nature of the electronic structure represents a more significant characteristic than the degree of BLA. It will be important to determine the length up to which the **ACn** compounds can retain full delocalization.

Supporting Information Available: Summary of the computational methods and an illustration of the frontier MOs of **C5** and **AC5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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