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The Use of Prochiral Centers for Demonstrating Asymmetric Stacking in Aggregates of Azulenylazulenium Cyanine Dyes

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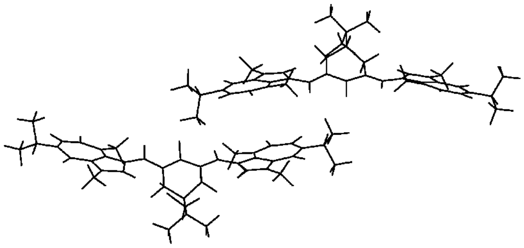
ABSTRACT



The diastereotopic methyl signals detected at low temperatures or high concentrations of an azulenylazulenium salt containing prochiral centers are consistent only with a model involving monomers in rapid equilibration with dimers in the staggered (“brickwork”) arrangement and not in the “card-stacked” arrangement.

Cyanine dyes and a number of other organic molecules featuring extended π-electron frameworks have large third-order optical nonlinearities and are potentially useful for electrooptical applications such as optical power limiting.[1] We have previously determined that azulenylazulenium carbocations, cyanine dyes with the nonalternant hydrocarbon azulene replacing heteroaromatic end groups as both the π-electron donor and acceptor (compounds **1** and **2**), have large third-order susceptibilities and are good power limiters.[2] There are many examples of the effect of molecular aggregation of cyanine dyes on their linear absorption in solid. Thus, the blue color of flowers (e.g., cornflower) is a manifestation of the interaction of the layered structure of anthocyanin dyes with light.[3] Similarly, chromophore stacking into well-ordered layer macro-structures contributes to enhanced optical nonlinearities in dyes.[4] Reliable structural information is more readily available in solids; in solution, such information is lacking. For dimeric aggregates in solution, two general structures have been postulated: the “card-stacked” and “brickwork” structures,[5] although their assignment was no more than by analogy with the corresponding crystal structures. We now wish to report on the detection of nonsymmetrical dimer aggregates of a series of azulenylazulenium carbocation dyes related to **1** and **2** by ^{1}H NMR spectroscopy. We believe the method is generally useful for studies of other aggregates in solution. It is the subject of this Letter.

In addition to azulenylazulenium salts (**1** and **2**), we have prepared compounds **3a**−**c** and **4**, by following established condensation reactions.[6] For specific information on **3** and **4** including their spectra, see Supporting Information.

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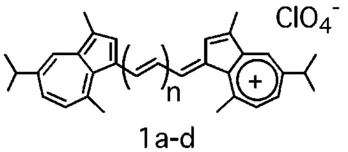
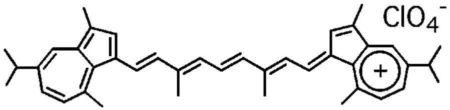


1a-d

1a: n = 0
1b: n = 1
1c: n = 2
1d: n = 3



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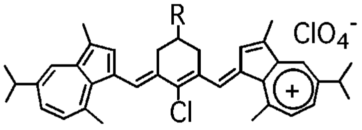
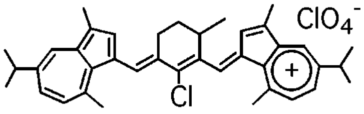


3a-c

3a: R = *t*-butyl
3b: R = CH_3
3c: R = H



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Room-temperature ^{1}H NMR spectra of all these salts show features expected of symmetrical ions; i.e., only one set of H-signals was observed for the two halves of each of the molecules (see: e.g., Figure 1, lower). At lower temperatures (0 to −90 °C), the spectra of compounds **1a**−**d** retained the same general features except for upfield shifts of nearly all H-signals in a manner similar to that reported for other cyanine dyes (e.g., compound **5**).[7] (For partial data of temperature shifts, see the Supporting Information). Compounds **3a** and **3b**, however, showed an entirely unexpected behavior. The simple isopropyl methyl doublet observed at room temperature switched to two sets of doublets with progressively larger $\Delta\delta$ at temperatures below −25 °C (see inset in Figure 1). (Because of solubility and solvent viscosity limitations, the low-temperature limit for this study was at −90 °C.) Significantly, no other signals of the salt showed any indication of splitting into two at any temperature, and it is particularly noteworthy that the splitting was not accompanied by line coalescence or line width changes normally associated with an activated process detected in a dNMR experiment.

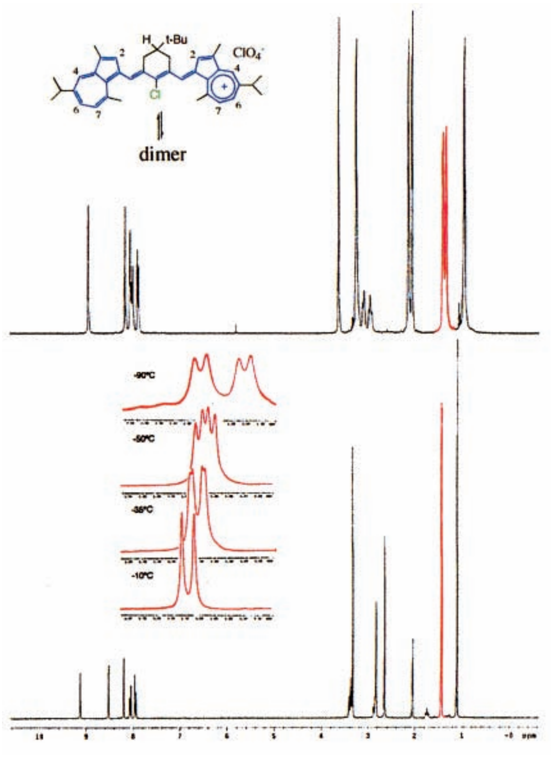
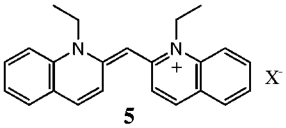


Figure 1. H NMR spectra of cyanine dye **3a** in acetone-d_6. Lower, at room temperature; upper, at −90 °C. Inset: expanded isopropyl methyl signals at −10 °C (lower) and −25 °C, −40 °C, and −90 °C (upper).



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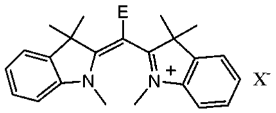


6: E = H
7 a-d: E = F, Cl, Br, I

Before considering the possible causes for the apparent temperature-dependent behavior of the isopropyl methyl signals, the following additional observations should be mentioned. First, the splitting of the methyls was in reality a concentration-dependent phenomenon: for the highest concentration sample (0.0080 M), the separation of the doublets became observable at ca. −50 °C while for the lowest concentration sample (0.00077 M) the splitting started at ca. −90 °C (see Figure 2 for the changes). Second, the temperature-dependent effect was solvent dependent: splitting was observed in both acetone-d_6 and acetonitrile-d_3 but

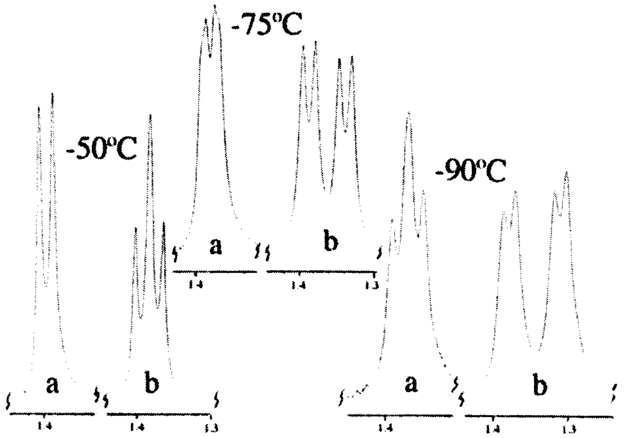
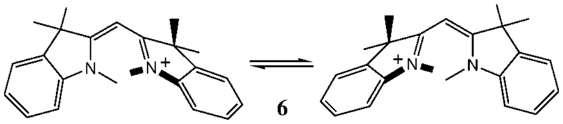


Figure 2. Concentration-dependent isopropyl methyl signals of **3a** (a) 7.7 × 10^{-4} M, (b) 8.0 × 10^{-3} M in acetone-d_6. Left, −50 °C; middle, −75 °C; right, −90 °C.

not in CD_2Cl_2 in which the salt is more soluble. Third, the splitting was also affected by the nature of the substituent on the central ring portion of the dye molecule. Replacement of the *tert*-butyl group in **3a** by a smaller methyl group (**3b**) lowered the temperature where splitting began to occur from −25 to −50 °C. Further replacement of the alkyl group by H (**3c**) eliminated the temperature-dependent phenomenon altogether; i.e., **3c** behaved like the symmetrical ions **1a**−**d**. Last, upon relocation of the symmetrically located 4-methyl group to the asymmetric 3-position (**4**), all chain and ring signals doubled in number while the splitting of the isopropyl methyls at low temperatures was unaffected.

Also, it is appropriate to compare the current result with the relevant temperature-dependent NMR results in the literature, particularly those reported for compounds **6**.[8] Only for the shortest member in the series (**6a**, $n = 0$) was the ^1H NMR spectra found to be temperature-dependent. The signal for the geminal dimethyl groups is a singlet at room temperature and a doublet at ≥40 °C. For halogenated analogues (**7a**−**d**), the coalescence temperatures were found to be above room temperature. The general behavior of the spectra followed that of an activated process for interconversion of two nonequivalent methyls: specifically the result of equilibration between the diastereotopic methyls in two nonplanar (sterically crowded) conformers (see below).



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The current result is clearly different from those of compounds of general structure **6** or **7**. First, for the shortest member of the azulenic cyanine dyes (**1a**), no temperature-dependent diastereotopic methyl signals were detected. Second, nonequivalent methyls were detected only for longer cyanine dyes, specifically those containing a prochiral center (**3a**, **3b**).

When these contrasting features are considered in light of the concentration-dependent phenomenon and earlier postulated dimeric aggregation of other cyanine dyes (such as **5**) in UV studies[7] and the aforementioned two common forms of stacked interactions, we believe the observation is consistent only with the following model: the symmetrical monomers being in rapid equilibrium with unsymmetrically stacked (brickwork) dimers (see graphical abstract). Most of the azulenic cyanine dyes (**1**−**3**) in this study have a 2-fold symmetry in which the isopropyl methyls are magnetically equivalent. However, for compounds **3a**,**b** where a prochiral center at C-4 exists, under conditions for aggregation (high concentration or low temperature), two sets of methyl signals of the isopropyl groups became observable. This is not believed to be due to nonequivalent isopropyl groups because all other signals of the two halves of the molecule remain identical. The only likely remaining possibility is the presence of an asymmetric center. Thus, we believe that in the aggregated form the C-4 center must have become chiral, induced by the unusual environment.

For the above-mentioned card-stacked and brickwork aggregates of cyanine dyes,[5] the former retains a 2-fold symmetry (Figure 3). Only the latter is consistent with the NMR data. The pattern of changes from a simple doublet of the isopropyl groups in the rt spectrum of **3a** to progressively separated two doublets at lower temperatures is only consistent with the view that the signals are simple averages of those of the monomers and the aggregated dimers *in rapid equilibrium*. Instead, in slow equilibrium, one would expect to see a separate isopropyl signal attributable to monomers and two sets of isopropyl methyl signals associated with the frozen aggregates of symmetrical salts **1** and **2** as well as those with a prochiral center, **3a**,**b**.

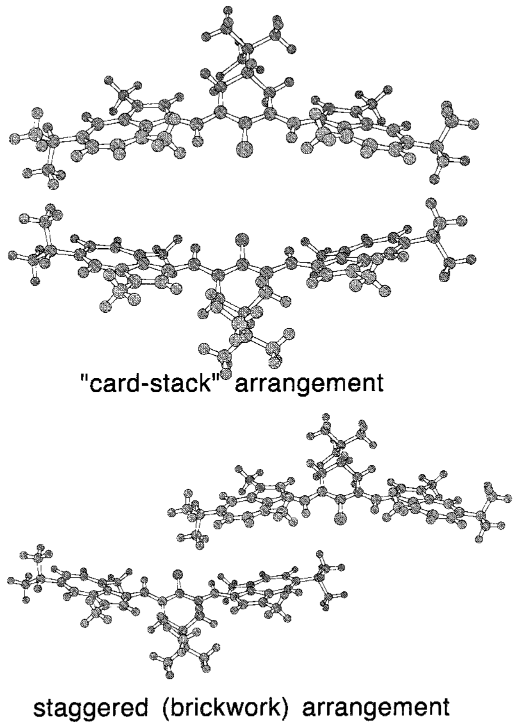

Figure 3. The proposed card-stacked and staggered (brickwork) dimer aggregates of **3a**.

Therefore, by way of this set of unusual temperature- and concentration-dependent NMR data, we believe we have found a simple method for distinguishing between the two aggregation structures in solution, or more specifically a method for detecting the unsymmetrical environment for a set of cyanine dyes. The method is potentially applicable to all other forms of aggregates where a prochiral center can be introduced. Also, the possible use of an aggregation-induced parameter for detection of molecular asymmetry as

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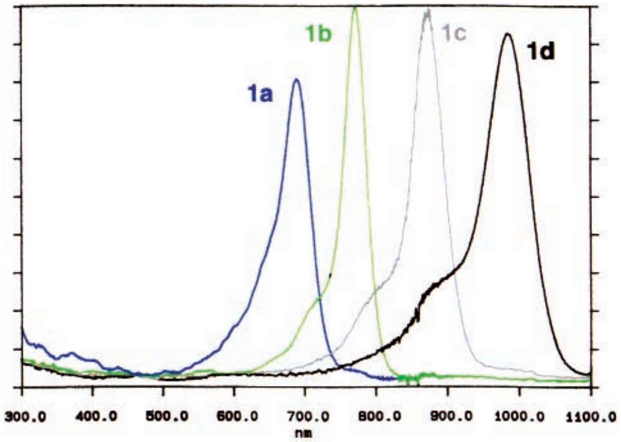

Figure 4. UV−vis absorption spectra of cyanine dyes **1a**−**d** in CD_2Cl_2. A dilute solution of **1d** is virtually colorless.

described above deserves further investigation. Quantitative experiments are in progress to determine the equilibrium constants of the proposed dimeric association. Also, it will be of interest to examine the possible use of such asymmetric aggregation and related polarized azulenic polyenes[9] in nonlinear optical studies.

In passing we would like to add that the cyanine dyes **1**−**4** show an expected sharp absorption band characteristic of cyanine dyes (Figure 4). They support the interpretation of formation of highly delocalized cations in the formation of NIR-absorbing azulenic bacteriorhodopsin analogues.[10] Furthermore, the absorption characteristics of the azulene chromophore allow ready preparation of NIR-absorbing pigments. Thus, the new pigment **1d** has an absorption maximum at 987 nm in dichloromethane.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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