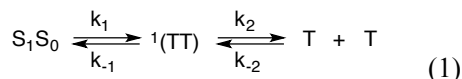


PRF#: 57843-ND4

Project Title: Acene Dimers: Synthesis, Structure, and Photochemical Properties

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Narrative: In this project, we proposed to synthesize a series of acene-derived cyclophanes that have differing distance and geometries between the two acenes. Once prepared, we will study the photophysical properties of these compounds to better understand energy transfer between excited state acenes. Our proposal focused on studies of singlet fission (SF) and related processes. Singlet fission occurs between two chromophores wherein a singlet excitation that is nominally localized and described as (S_1S_0) undergoes a non-radiative conversion to a singlet-coupled pair of triplets ($^1(TT)$). This multi excitonic state can then convert to uncorrelated electronic excitations, $T + T$ (Eq 1). This process can be rapid, provided that it is not significantly endergonic and that electronic coupling between the chromophores is favorable. To have favorable energetics, the energy of S_1 should be at least twice that of T_1 .



This process is spin allowed and can proceed via two pathways. One is dubbed “electron transfer” (Figure 1), the other “hole transfer” (not shown). In the “electron transfer” coupling, the excited electron in chromophore A is transferred to the LUMO of chromophore B and a ground state electron in chromophore B is transferred to the LUMO of chromophore A. By the hole transfer coupling, a ground state electron of chromophore B is transferred to the HOMO of chromophore A, and the other HOMO electron of chromophore A is transferred to the LUMO of chromophore B (Figure 1, right). Both pathways proceed via charge transfer (CT) states (i.e., the initial state wherein an electron has been transferred) that are virtually occupied during the energy transfer. These CT states can be coupled to both the starting state (S_1S_0) and the product ($^1(TT)$), and it is this coupling that permits the reaction to proceed and that we are probing using the molecules that we are synthesizing in this proposal.

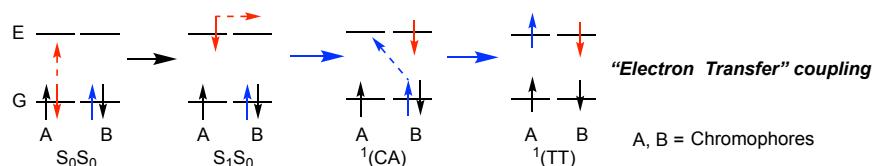


Figure 1

There are a relatively small number of chromophores that have the requisite energetics between S_1 and T_1 for efficient SF, with the most studied being the acenes, which are linear polyaromatic hydrocarbons. For longer acenes such as tetracene and pentacene $2xT_1$ is either close to the energy of S_1 or lower, rendering SF a potentially favorable process, so long as there is sufficient coupling between the chromophores.

In this proposal, we ask how spatial orientation and distance of chromophores impact the coupling and energy transfer among excited states in molecules that contain two chromophores. To answer this question, we proposed to synthesize a series of bis-acene cyclophanes wherein the distance and geometry between the two acenes is systematically varied. A generalized rendition of the desired cyclophanes is shown in Figure 2 below. Note that

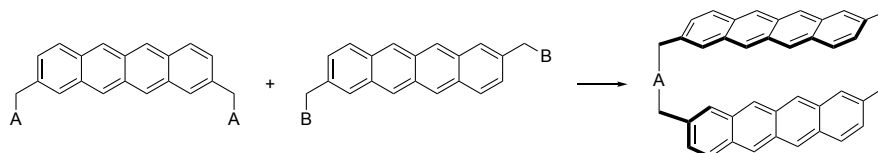
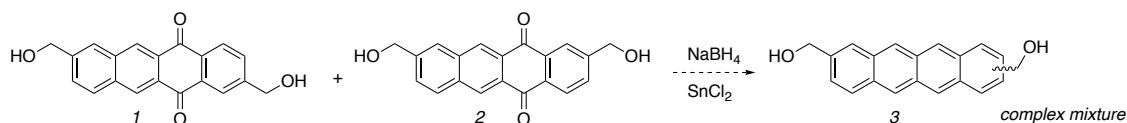


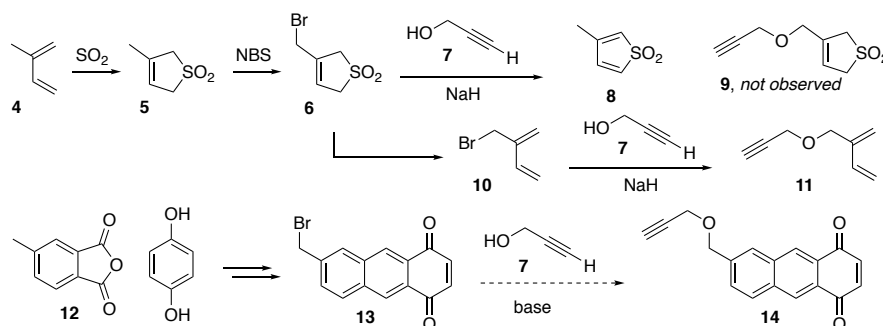
Figure 2

the linker, “A”, can be varied to adjust the distance and geometry of the acenes relative to each other. Once synthesized, the geometry will be determined by crystallographic methods and the rate and extent of photophysical processes measured to determine and better understand the geometric factors that influence SF. In the prior year’s report, we had prepared the functionalized quinone diols **1** and **2** as a mixture of isomers. These compounds were subjected to SnCl_2 -promoted reduction in an attempt to produce the corresponding tetracene derivatives (**3**), but these transformations were complicated by issues of solubility and reactivity, and produced complex mixtures (Scheme 1). Our goal in the most recent funding period was then to study this reduction in hopes of coaxing it to proceed in useful yields. Strategies pursued included variations in the conditions for the SnCl_2 step and functionalization the diols of compounds **1** and **2** in order to enhance solubility. The former included variations of the solvent, pH, and reaction time and temperature, but were not promising and as such this approach was abandoned. The latter included studies directed at the synthesis of a functionalized



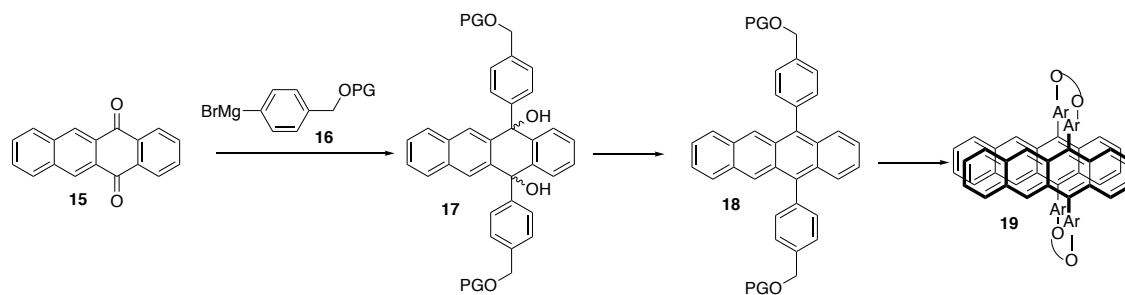
Scheme 1

quinone with substitution that would enhance solubility as well as allow for efficient coupling of the resulting acene to provide the desired cyclophanes. Attempts to follow a route analogous to that used to prepare the diene required for the synthesis of compound **1** (see prior progress report) were pursued; however, subjecting compound **6** to etherification with propargyl alcohol provided the elimination product **8** under all conditions studied (Scheme 2). In contrast, conversion of bromo-sulfone **6** to bromo-diene **10** smoothly provided the desired diene-yne product **11**. This species was to be subjected to a Diels-Alder reaction with quinone **14**; however, access to **14** was limited as mild substitution conditions (carbonate base or weaker base + alcohol) provided recovered starting material and no discernable product. More forcing conditions (alkoxide base) provided a complex mixture. Ultimately, low yields of product were obtained upon treatment of **13** with AgNO_3 and the corresponding alcohol as solvent. We speculate that the issue with more forcing conditions is due to the electrophilicity of the quinone as a competitive reaction path to nucleophilic displacement of the bromide. Ultimately, this route was deemed impractical and was abandoned.



Scheme 2

While the structures we have devised will accomplish the goal of studying energy transfer in well-defined systems, our experience has led us to consider structures that would not suffer the reactivity or solubility issues we have encountered to date. We also wished to avoid the regioisomeric issues of compound **3** and related derivatives. As such, we have turned our attention to the synthesis of the related cyclophanes **19**. Space limitation preclude a detailed discussion, however, the general path being pursued is described in Scheme 3 below. Addition of aryl Grignard reagent **16** to quinone derivative **15** would provide diol **17** which upon subjecting to reduction would provide acene **18**. Deprotection would provide a diol that can be functionalized with a bis-electrophile to provide the desired cyclophane, **19**.



Scheme 3

Impact: This award has allowed me and the graduate student working on this project to explore a new avenue of research that would otherwise not be possible. Further, we are now poised to study physical organic chemistry and photochemistry in collaboration with the co-PI on this project that neither of us individually could pursue due to our complementary sets of expertise. In this respect, this collaboration has been scientifically enabling. Finally, the impact on the graduate student working on this project has been substantial as this work has exposed him to new areas of science, especially issues in the design of molecules for energy transfer, to which he would not otherwise not have been exposed.

Publications: None in the prior funding period.