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X-ray Structure of a CT Complex Relevant to Diels−Alder Reactivity of Anthracenes

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Anthracenes, as well as acenes, are known to undergo Diels−Alder (DA) addition on their central ring (*i.e.* at the 9- and 10-positions) with a variety of dienophiles.[1] Such reactions have attracted recent attention in the fields of dynamic covalent chemistry,[2] chiral induction,[3] and fullerene functionalization.[4] In the early reported cycloaddition of electrodeficient dienophiles to anthracene, formation of transient charge transfer complexes (CTCs) has been observed in solution.[5] The properties of these strongly colored CTCs, together with their possible role as reaction intermediates, have been discussed extensively, but their characterization in the solid state has been rarely reported.[6,7]

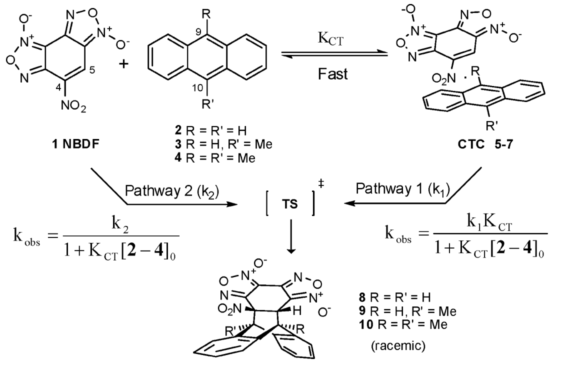
In this regard, several authors have pointed out that a successful X-ray characterization of CTCs would help considerably to delineate the reaction coordinates of the related DA reactions.[7a−d] Based on the few reported X-ray structures of CTCs in DA reactions of anthracenes, it has been suggested that the formation of these complexes facilitates the overall DA reactions. To be noted is that most of the reported physical studies have involved highly symmetric dienophiles, i.e., TCNE,[6−8] maleic anhydride,[9] and dithiins, and no data have been reported so far for highly electrophilic systems such as nitroolefins.[6−11]

A recent ranking of 4-nitrobenzodifuroxan **1** (NBDF)[12] on Mayr's electrophilicity scale[13] has revealed that the reactivity of the nitro-activated double bond of this peculiar olefin surpasses that of commonly activated C═C double bonds by several orders of magnitude.[14] Thus, superelectrophilic properties have been accorded to NBDF,[14] making it of particular interest to investigate its DA reactivity as nitroolefin toward anthracenes.

Here, we report on a comprehensive structural, thermodynamic, and kinetic study of the interactions of **1**, with the three anthracenes **2**−**4**, which proceed with high stereoselectivity to afford exclusively the diastereomers **8**−**10** (Scheme 1). A most significant result of this study is the X-ray-single-crystal analysis of the complex **5** isolated from the interaction between **1** as the dienophile and **2** as the aromatic diene. This overall process is compared to that of TCNE and anthracenes **2**−**4** reported in the literature, a well-known case of a "CTC" assisted DA reaction.[6−8]

A deep green color appears spontaneously upon mixing of chloroform solutions of NBDF **1** (1 equiv) and each of the three anthracenes **2**−**4** (1 equiv). Interestingly the color persists overnight in the case of anthracene **2**, while it disappears in a few minutes in the case of 9-methylanthracene **3** and 9,10-dimethylanthracene **4**. Clearly the overall cycloaddition sequence proceeds much more rapidly with the electron-rich anthracenes **3** and **4**; nevertheless UV−visible spectra of CTCs **5**−**7** could be recorded in solution as well as in the solid state for **5** (Figure 1b), showing a strong absorption of these species in the wavelength range 510−630 nm where neither NBDF **1** nor the anthracenes absorb.

Scheme 1



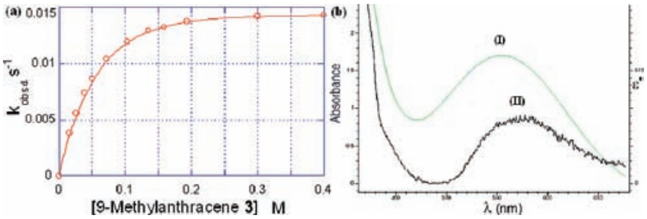


Figure 1. (a) Effect of the concentration of **3** on the observed rate of formation of the cycloadduct **9** in $CHCl_3$ at 25 °C. (b) UV−visible spectrum of the CTC **5** in $CHCl_3$ (curve I) and in the solid state (curve II).

Table 1. Thermodynamic Data for Formation of the CTCs **5**−**7**[a]

	NBDF (EA = 2.45 eV)[b]			TCNE (EA = 2.88 eV)[c]		
CTC	K_{CT}	$\Delta H°$	$\Delta S°$	K_{CT}[d]	$\Delta H°$[d]	$\Delta S°$[d]
5	5.5 ± 0.3	−4.5	−14.0	1.73	−2.7	−8.0
6	20.8 ± 0.7	−5.4	−14.0	18−25	−4.3	−9.6
7	28.0 ± 0.9	−3.0	−3.0	130[e]	−5.6	−12.7

[a] A detailed analysis of the data leading to K_{CT} (in M^{-1} at 25 °C in $CHCl_3$), $\Delta H°$ (kcal·mol^{-1}) and $\Delta S°$ (e.u.) values is given as Supporting Information (SI). [b] EA calculated according to Mullikens's equation; see SI. [c] Reference 1. [d] Reference 8a−8e. [e] Estimated in reference 8c.

Using Job's method of continuous variations, the 1:1 stoichiometry of the CTC **5** was readily established.[15] Concomitantly the equilibrium constants K_{CT} for formation of the CTCs **5**−**7** were determined spectrophotometrically together with the related enthalpies and entropies associated with this process ($\Delta H°$, $\Delta S°$). Comparing these data (Table 1) with those previously reported for the interactions of anthracenes **2**−**4** with TCNE revealed that the stability of our CTCs is rather similar.[8] Interestingly the electron affinity (EA) of NBDF (2.45 eV) is found to be slightly lower than that of TCNE (2.88 eV).[1b]

The interaction of NBDF **1** with 9-methylanthracene **3** could be kinetically investigated at 25 °C in chloroform. A major feature (Figure 1a) is the curvilinear dependence of the observed rate constant $k_{obsd.}$ for the cycloaddition process that has been measured by following the disappearance of the CTC **6** upon the anthracene concentration. As elaborated previously for a number of DA reactions involving an electrodeficient dienophile,[7,8] such a saturation behavior implies that the cycloaddition sequence leading to the product **9** proceeds via an initial and fast formation of the CTC **6**. Because the rate equations (Scheme 1) pertaining to the two possible mechanistic pathways depicted in Scheme 1 are formally similar, the data obtained do not allow to ascertain whether

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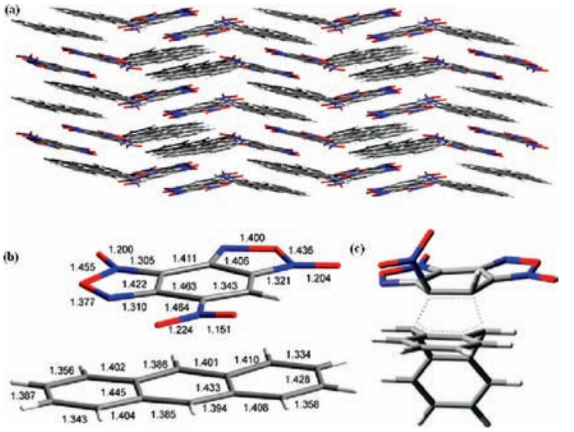

Figure 2. X-ray structure of CTC **5**. (a) Side view of the unit cell along the *a* axis. (b) Bond lengths in Å of **1** and **2** in CTC **5**. (c) Calculated DFT structure of the corresponding DA transition state at a B3LYP level.

the CTC is an intermediate on the reaction coordinate leading to **9** (pathway 1) or is formed in a side, and therefore nonproductive, equilibrium (pathway 2). In a study of the reaction of TCNE with 9,10-dimethylanthracene **4** at different temperatures, Kislev and Miller have found an overall negative enthalpy of activation ($\Delta H^{\#}_{\mathrm{exp}}$) and suggested that this particular situation is only consistent with the corresponding CTC being an intermediate on the reaction coordinate.[8c] It appears that the above reaction is the unique case where the intermediate CTC is stable enough to exhibit a large negative enthalpy of formation ($\Delta H°$) value which overcomes the activation energy ($\Delta H^{\#}$) value pertaining to the cycloaddition step.[7f,8c] Apart from this exception, it remains that DA reactions are associated with positive $\Delta H^{\#}_{\mathrm{exp}}$ values so that thermodynamic and kinetic studies are mechanistically unconclusive.[7−9] No negative values of $\Delta H^{\#}_{\mathrm{exp}}$ were here determined for the reaction of **2**, **3**, or **4** with NBDF **1** (1.1, 8.8, and 12.2 kcal.mol^{-1} respectively) so that no conclusion regarding the preferred pathway in Scheme 1 can be drawn.

A most informative result has come from the isolation of a stable crystal, suitable for an X-ray analysis, upon evaporation of a chloroform solution of CTC **5** under a flow of argon. In Figure 2, the X-ray structural determination confirmed the formation of the anticipated **5** as a face to face $\pi-\pi$ complex with a 1:1 donor−acceptor ratio. The cofacially oriented anthracene and NBDF moieties afford infinite alternate stacks along the crystallographic *b*-axis with a close interplanar distance of 3.45 Å.

Because of the facile subsequent formation of the corresponding cycloadducts, it is only in very few instances that CTCs involved in the reaction of anthracene with electrodeficient dienophiles could be successfully characterized by X-ray.[10,16] It is therefore a significant result that the X-ray structure of **5** is the first example of CTCs in which the diene **2** and the dienophile **1** lie in a parallel arrangement and are not suitably preoriented for a direct conversion to the expected cycloadduct **8**.[16] The X-ray data indicate that the NBDF moiety is not appreciably altered upon complexation, ruling out a possible mechanism with a single electron transfer. Interestingly, there is no structural relationship between the X-ray structure, where **1** and **2** are probably oriented according to Mulliken's "Overlap and Orientation" principle,[17] and the optimized DFT structure of the TS, where secondary orbital interactions between the **1**-LUMO and the **2**-HOMO are ideal for a DA reaction. In fact, the anthracene moiety has to rotate 75° to adopt the orientation required for the cycloaddition. Obviously, this situation does not support the assumption that CTCs resemble the TS in DA reactions. It also reveals that the CTC has to dissociate back to the reactant, allowing the two partners to undergo cyclization through another different prereaction complex.

This conclusion is consistent with the information derived from recent quantum calculations,[18] secondary isotopic effects analysis,[8a] and nonsteady-state analysis,[19] which point out that CTCs are not transition state-like, even when the reaction centers in the CTC are ideally positioned to achieve the cycloaddition.[18,19]

X-ray-single-crystal analyses performed on crystals of **5** after 6 months of storage show no chemical transformations. As a consequence, no solid-state topochemical DA reactions can be envisioned in our CT crystal. Obviously, substantial CT stabilization inhibits the DA reaction in the crystalline state. Even if it is still difficult to conclude on the role of the CT interactions in solution, and therefore on the preferred pathway of the DA reaction, the X-ray analysis of the intermediate CTC is of primary importance in the field of DA reactions and further experimental efforts are being carried out.

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Supporting Information Available: Crystallographic data for **5**; HRMS and NMR for **8**−**10**; Determination of electron affinity of **1** and kinetics procedures and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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