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Photo Retro Diels-alder Reaction Of The Adducts Of Tetracyanoethylene And Polyaromatic Compounds

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PHOTO RETRO DIELS-ALDER REACTION OF THE ADDUCTS OF TETRACYANOETHYLENE AND POLYAROMATIC COMPOUNDS

by

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ABSTRACT

Thermally induced retro-Diels Alder (rDA) reaction has been extensively used for the preparation of many reactive intermediates in organic synthesis. But the uses of photo-retro Diels-Alder (PrDA) reaction in organic synthesis were sparingly reported in literature. Due to its spatial and temporal control, PrDA can be used in making of photosensitive materials, in drug delivery and also for mechanistic studies. Diels-Alder adducts of tetracyanoethylene (TCNE) and polyaromatic compounds (anthracene, napthacene, pentacene and phencyclone) were synthesized and were subjected to PrDA reaction through 254-nm irradiation. The quantum yield and the consequent photoreactivity of these DA adducts follow the following order.

TCNE/naphthacene > TCNE/anthracene ≥ TCNE/pentacene

This trend was explained by a mechanism of charge-separated intermediates. The stability of the charge-separated intermediate is the governing factor of this trend of photoactivity of DA adducts. Based on these results it is possible to design a proper DA adduct and consequently predict the feasibility of the PrDA reaction.

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To my mother and to my younger brother, for their endless support and encouragement.

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CHAPTER ONE: INTRODUCTION

1.1: Diels-Alder Reaction-an overview

Figure 1 Otto Diels (1876-1954)

Figure 2 Kurt Alder (1902-1958)

The Diels-Alder (DA) reaction is one of the most extensively used reactions in organic synthesis. For many years this reaction has been utilized in developing of organic reaction intermediates and widely applied to study pericyclic reactions. This reaction was first discovered (in 1920's)

by two German Chemists, Otto Diels and his student Kurt Alder. For their discovery, this reaction has received a name of "Diels-Alder Reaction". The versatile applicability of the DA reaction in synthetic organic chemistry fetched the Nobel Prize award in Chemistry in 1950 to these scientists. To illustrate a detailed mechanistic explanation of DA reaction, addition reaction (Fig3) between a 1, 3-diene and an alkene (called a dienophile) is used.
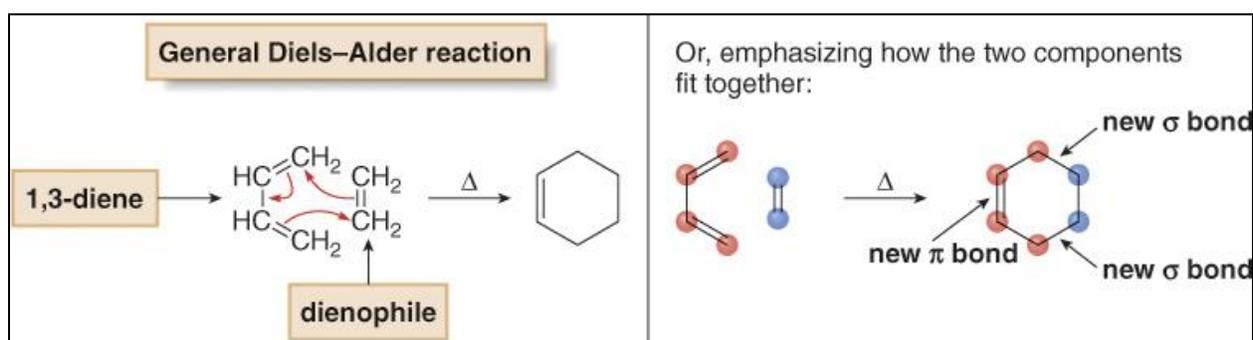
Figure 3 Schematic representation of Diels-Alder reaction (adapted from Organic Chemistry by Donald Mc Murry)

The cyclic movement of electron pairs in between diene and dieneophile are shown by curved arrows (Fig3). In the course of DA reaction two σ bonds and a π bond are being formed with the breakage of 3π bonds. Since one σ bond is ~20 kcal/mol stronger than a π bond, it is expected that in a DA reaction will release ~40 kcal/mol of energy. In a typical DA reaction, a cycloaddition reaction occurs between diene and dienophile. To get an effective cycloaddition, in most cases Dienophiles are substituted with electron withdrawing groups (such as nitrile, ester or carbonyl, etc). In terms of reaction mechanism of the DA reaction, it is well established that a clycloaddtion reaction takes place due to a parallel overlap of π electron clouds of diene and dienophile. This phenomenon is explained by Frontier Molecular Orbital Theory (FMO). Based on the FMO approach, DA reaction can be seen as an effective interaction between the diene's

highest unoccupied molecular orbital theory (HUMO) and dienophiles lowest unoccupied molecular orbital (LUMO) (Fig4). The energy difference between these two orbitals plays the pivotal role in determining the effective interaction of electron clouds. The lower the energy difference, the higher is the interaction and the greater is the chance of formation of DA adduct.
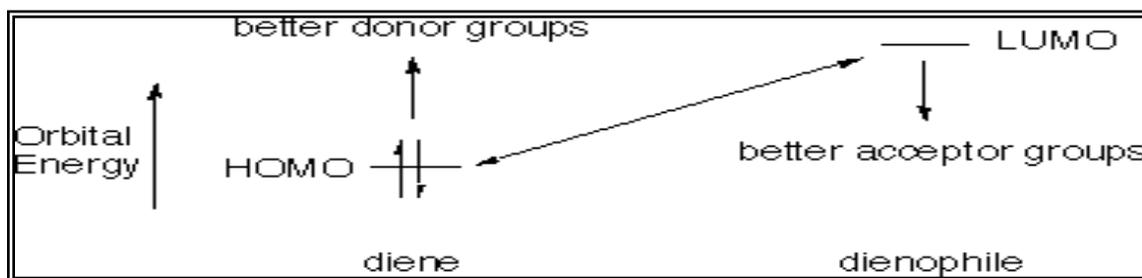
Figure 4 Molecular Orbital Representation of Diels-Alder Reaction

1.2: Retro Diels-Alder reaction

With the help of a proper driving force, the Diels-Alder reaction can run in reverse direction, which will produce two separated species, generally a diene and a dienophile. These species can be generated exactly from starting material containing a cyclohexene ring. The stable production of separated diene and dienophile from a DA adduct is known as retro-Diels-Alder Reaction (rDA) (Fig5).

Figure 5 Schematic Representation of Retro-Diels-Alder Reaction

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The most prominent example was the decomposition of adducts of cyclohexadienes with acetylenic dienophiles to produce an olefin and an aromatic compound[3] (Fig6).

DA reaction between cyclohexadienes with acetylenic dienophiles to produce an adduct and then decomposition of that adduct to produce an olefin and an aromatic compound olefin and an aromatic compound
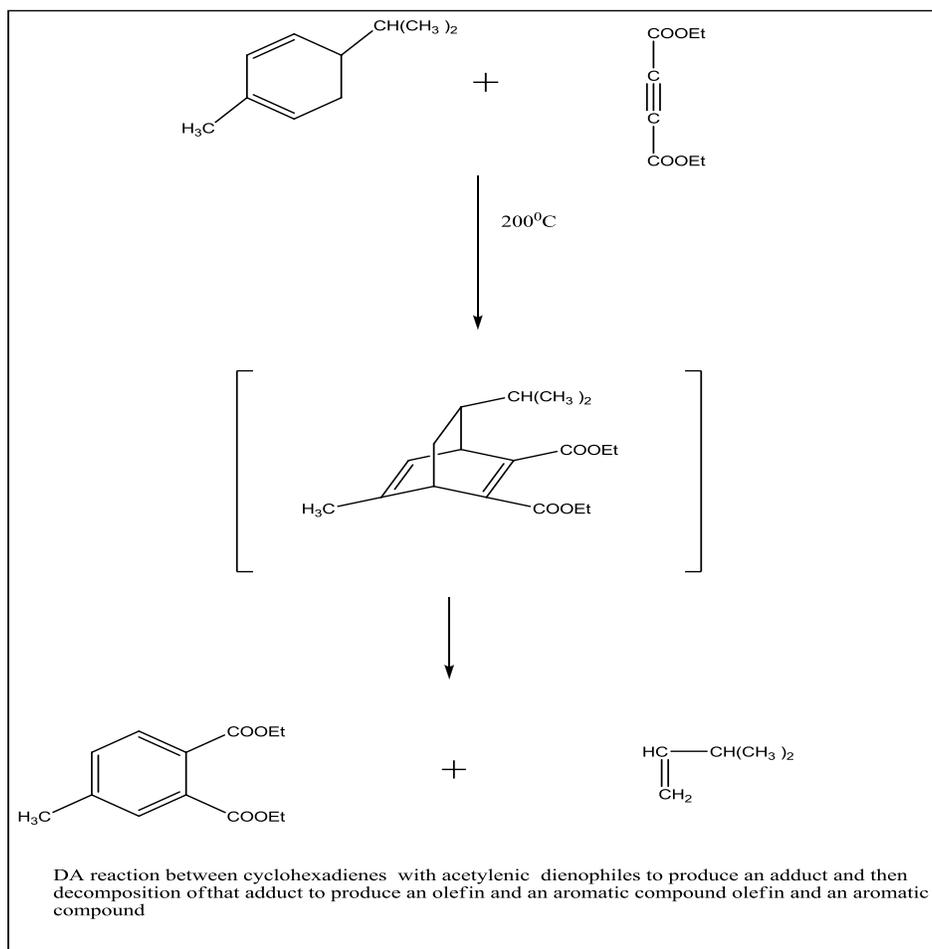
Figure 6 Example of a Retro-Diels-Alder Reaction (Ref-3)

1.2.2: Structural effect on the rate of retro Diels-Alder reaction

The prediction of temperature at which a specific rDA reaction can take place is very difficult. In order to achieve a feasible rDA reaction it is imperative to understand the factors- which might

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influence the course of rDA reaction. Substituents at Diene or Dienophile have immensely influenced the rate of rDA reaction. A survey of substituents effects of rDA reaction has been reported[4]. Anthracene is widely used in DA reaction as a Diene but many other polycyclic aromatic compounds can also be added to dienophiles. In general any aromatic compound can add to dienophiles. Aromatic rings of these compounds may or may not form a Kekule structures[28]. Bachmann and Kloetzel[29] used maleic anhydride (as a dienophile) with a number of polycyclic aromatic compounds (diene) in boiling xylene in a 1:1 mole ratio. In some cases, the reactions were unable to reach completion but were successful to achieve equilibrium. Bachmann and Kloetzel, did couple of reaction by varying the subtituents at diene and kept the same dienophile (maleic anhydride) in 1:1 ratio. Based on these results they constructed a chart (table 1) which shows the % of adduct at equilibrium for a number of different polycyclic aromatic compounds. This chart explains importance of the structural effects on regulating the relative proportions of the forward and reverse Diels-Alder reactions

Table 1 Effect of Various Substitutions on Diene at Diels-Alder Reaction (Ref-3)

Diene	% adduct
Anthracene	99
9-Methylanthracene	99
9,l0-Dimethylanthracene	98
Phenylanthracene	75
9, 10-Diphenylanthracene	16

From the Table-1, it is apparent that substituents on diene have great influence in the formation of DA product. I would like to discuss extensively the substituent effect on diene and dienophile in DA and in rDA reactions in the following sections.

Anthracene(Diene)   mono-subs ethelene(Dienophile)

heat

DA adduct

R

various substituents at dienophile

a,R=H
b,R-Me
c,R=i-Pr
d,R=iBr
e,R=Ph
f,R=SMe2
g,R=COOH
h,R=CONH2

f,R=COOR
h,R=CN
i,R=COR
j,R=CHO
k,R=NO2
l,R=OAc

DA reaction between Anthracene and mono-substituted ethelene
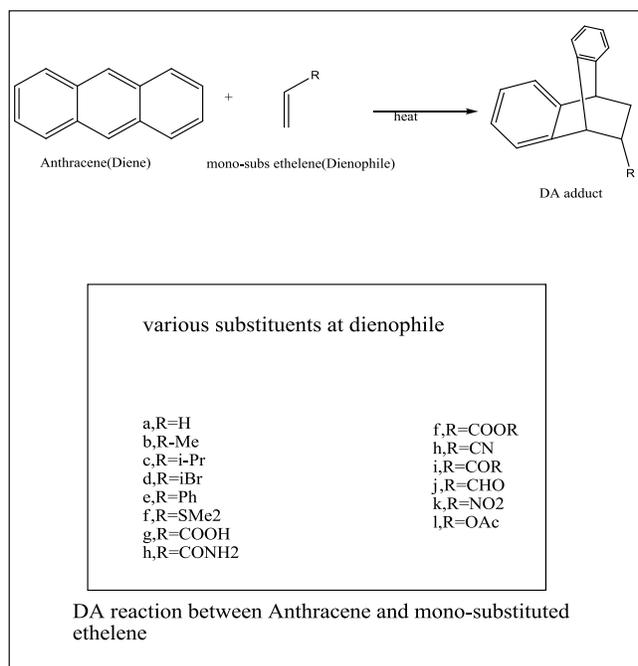
Figure 7 Diels-Alder Reaction and Effects of Substituents at Dienophile (Ref-4)
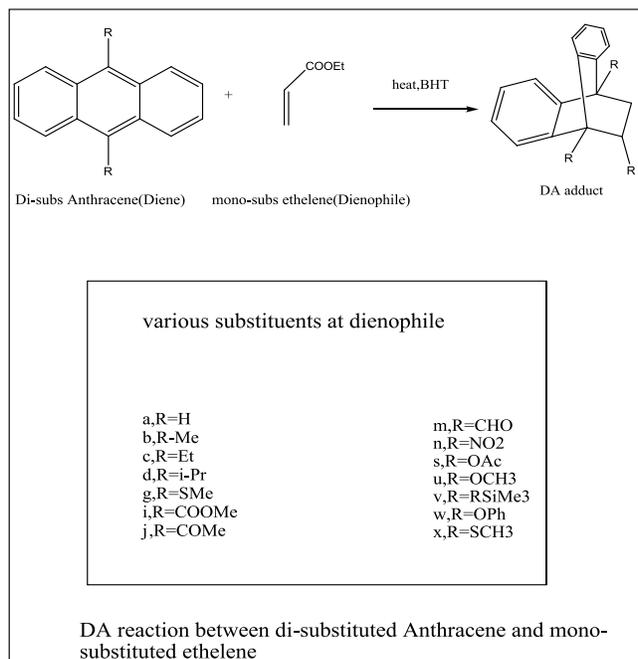
Figure 8 Diels-Alder Reaction and Effects of Substituents at Diene (Ref-4)

These sets of reactions in Fig-8 and Fig-9, clearly demonstrate that electron rich diene and electron deficient dienophile can enhance the rate of DA reaction. In practice, the rate of rDA reaction can also be accelerated by the use of electron rich diene and electron deficient dienophile[4]. The rate of rDA reaction of a DA adduct (formed by the reaction between Anthracene and substituted ethelene) cab be accelerated by an electron withdrawing substituents (on dienophile) to a large extent[4]. In this case, the acceleration of rDA reaction as compared to 1(H;a) is to the factors of 140 (COOH;g), ~40 ($CONH_2$; h) and etc[4]. On the other hand, electron donating substituents at diene are able to enhance the reverse reaction as compared to 1(H;a) by the factors ~40 (SMe ; g), ~2400 (NH_2 ; s) and so on[4]. Thus it is possible to accelerate the rate of

rDA reaction of a DA adduct by a placing electron donating and electron withdrawing substituents over diene and dienophile consequently.

1.2.3: Photochemical Retro-DA (PrDA) Reaction

Most of rDA reactions requires heat as a driving force for the reversion or dissociation of DA adduct. Thus generally rDA reactions are thermal. But in practice, photo-reversion can also be achieved with an appropriate absorption of light by DA adduct. Woodward-Hoffman rules[16] sates that for a rDA reaction it is necessary to follow a concerted mechanism. This kind of reaction pathways (i.e, concerted) is thermally allowed and photochemically forbidden. Despite of this assumption rDA reaction through a step-wise mechanism can be possible by photo process. The detailed picture of reaction mechanism of photo rDA (PrDA) reaction is not clear, because it has been sparsely reported in the literature.[7,17-19] For instance, Nozaki and Kato showed that DA adduct of anthracene and styrene yielded anthracene through photo irradiation, while on contrary an adduct of anthracene and 2-butene is photostable.[18] Jones et al. performed PrDA reactions of a chiral compound and showed the use of this reaction as a chiral auxiliary.[17] These sporadic examples of PrDA reactions are available, but a systematic study (theoretical or experimental) of the reaction mechanism of PrDA reactions is not reported in literature. A comprehensive knowledge of reaction mechanism and an idea of quantum yield of PrDA reaction will help to predict the feasibility of a PrDA reaction. Photo reaction allows spatial control in the nanometer range. This unique advantage of PrDA reaction over rDA reaction can be utilized into various domain, such as photo patterning, photolithograph, and drug delivery

etc.[15] The lack information about PrDA reaction obstructs its wide application in organic synthesis and in materials science. Photochemical addition of maleic anhydride to 9-methoxyanthracene produces compounds (2) and (3) [17]. Compound (2) dissociated into it's parent diene and dienophile. This is a unique example of PrDA reaction in recent times.
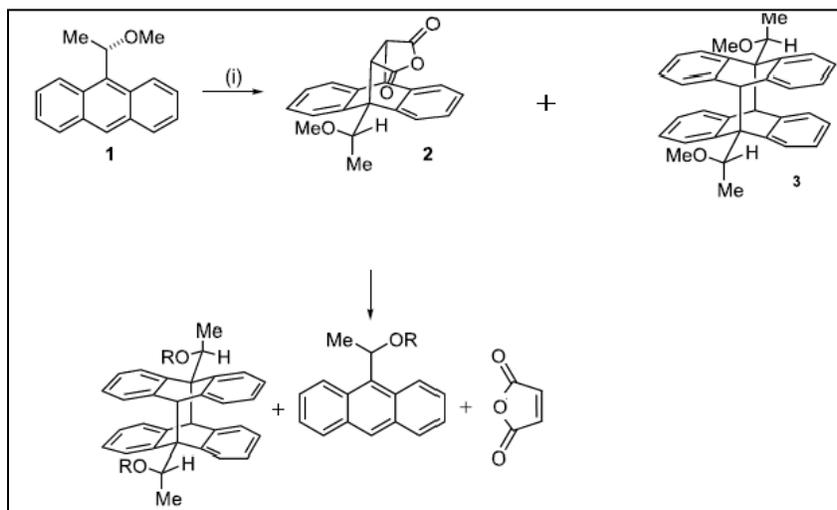
Figure 9 Example of a PrDA Reaction (Ref-17)

1.2.4: Positive aspects of Photo r-DA reaction over thermal r-DA reaction

a) Photo rDA reaction proceeds through an unimolecular process and is not affected by diffusion rate.

b) Yield is very high in solid state, which makes PrDA reaction useful for material application.

c) Spatial control is achievable. d) PrDA reaction can proceed without the addition of catalyst, acids or bases.

CHAPTER TWO: OBJECTIVES

DA adducts of tetracyanoethylene (TCNE) and polyaromatic compounds including anthracene, naphthacene and pentacene (Figure 1) were synthesis and PrDA reaction were performed. Due to the presence of strong electron withdrawing group, TCNE acts as a good dienophile.
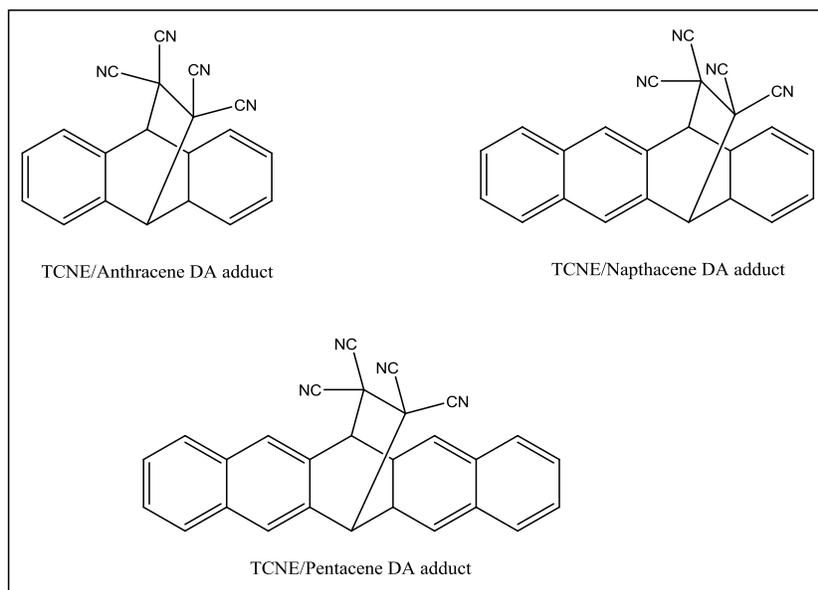
Figure 10 Diels-Alder adducts of Tetracyano Ethylene and different Polyaromatics

According to Woodward-Hoffman rules, a PrDA reaction must proceed via a step-wise mechanism unless the reaction is a non-adiabatic process. The step-wise mechanism can be either charge-separated or biradical. Therefore, we infer that if a DA adduct can absorb the irradiating light and stabilize the charge separated or biradical intermediate state the DA adduct could be photoreactive. The aromatic structure can both absorb light and stabilize charge via resonance structures. TCNE, with four strong electron-withdrawing CN groups, can stabilize negative chargestabilize negative charge in the intermediate state. Therefore, it is expected that PrDA reaction will occur due to a readily available charge separated intermediate state.
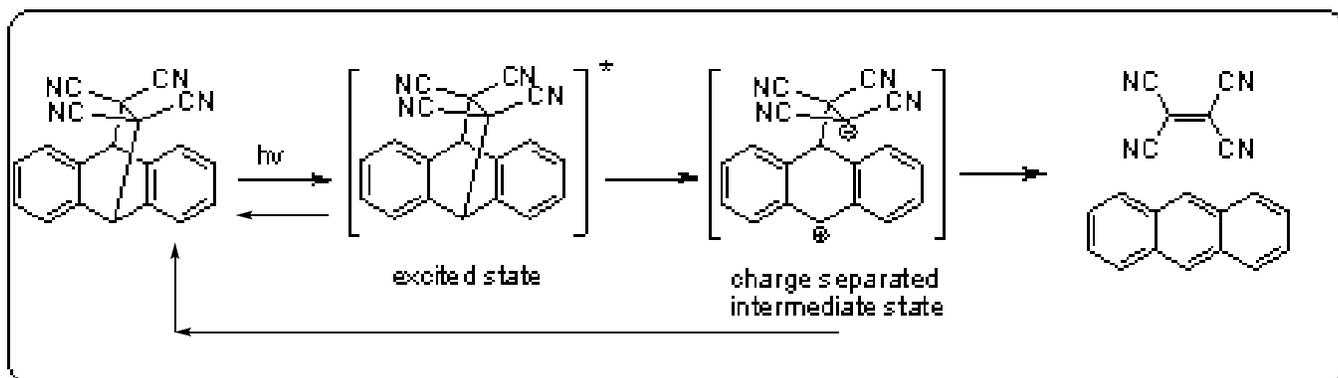
Figure 11 Mechanism of PrDA Reaction of Anthracene/Tetracyano Ethylene Diels-Alder Adduct

CHAPTER THREE: RESULTS AND DISCUSSION

3.1: An Overview

One of most intriguing aspects of the chemistry of anthracene is the ability to undergo both thermal and photochemical Diels-Alder cycloaddition with a variety of dienophiles across the 9 and 10 positions. At the very beginning of this project we made TCNE adduct of Anthracene and then tried to investigate the P-rDA reaction of this adduct. After getting a positive result we made other adducts of TCNE with a series of polyaromatics, including napthacene, pentacene and phencyclone. Our main objective was to study the P-rDA reaction of these adducts as the photoreactivity of these adducts can be extensively used to make photoresponsive materials. Acenes (especially napthacene and pentacene) are regarded as good organic electronic materials and also as a good fluorophores in solution[26]. Due to it's strong electron withdrawing property, TCNE can be used as an n-dopant or as an oxidant. A successful P-rDA reaction of TCNE/acene adducts will allow releasing the acene and TCNE with an available special control. This interesting characteristics of TCNE/acene adducts can be properly used in electronic materials,

fluorimetry and mechanistic study. Now for a feasible P-rDA reaction of TCNE/Polyaromatic compound, it is absolutely necessary to get a stable separated diene and dienophile. According to Woodward-Hoffman rules, a PrDA reaction must proceed via a step-wise mechanism unless the reaction is an adiabatic process. The step-wise mechanism can be either charge-separated or biradical. Therefore, we infer that if a DA adduct can absorb the irradiating light and stabilize the charge separated or biradical intermediate state the DA adduct could be photoreactive. As, it is well demonstrated that aromatic compound can absorb light and are able to form a stable charged species via resonance. On the other hand, TCNE with four electron withdrawing group will help to stabilize the negatively charged intermediate (formed after photo absorption). Therefore it is possible to run a P-rDA reaction due to the formation of a stable charged intermediate species (Fig-12). From the above discussions it is quite evident that the selection of a proper diene and dienophile is very important.

TCNE/Anthracene DA adduct

TCNE/Napthacene DA adduct

TCNE/Pentacene DA adduct

excited state

charge separated
intermediate state
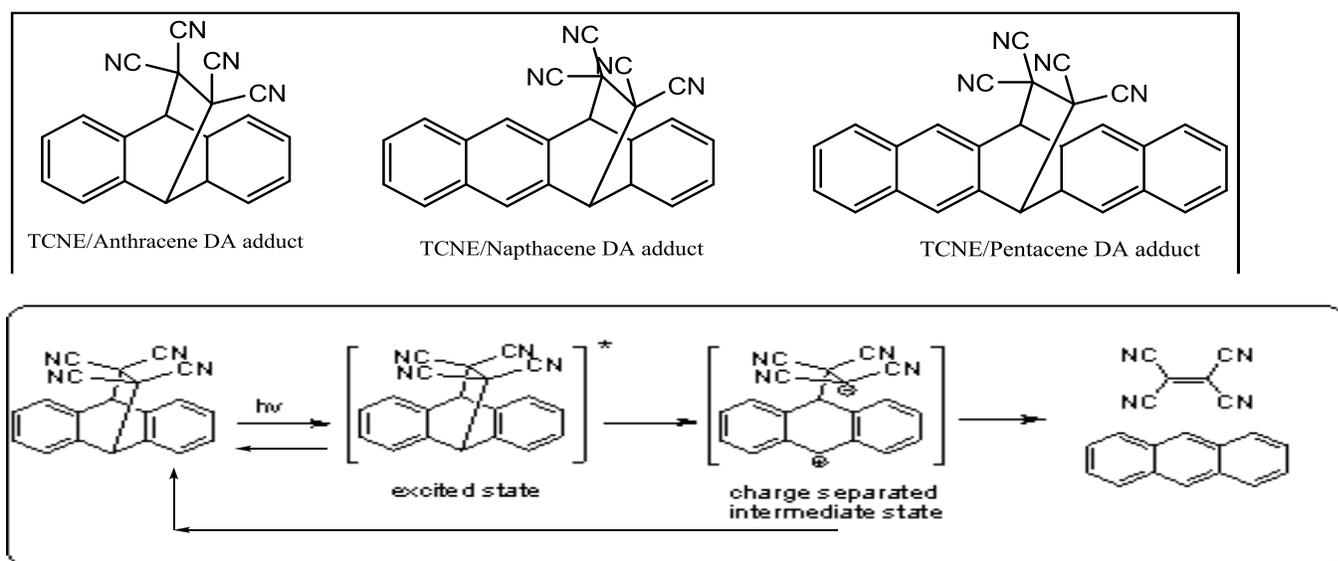
Figure 12 Structures of TCNE/anthracene, TCNE/naphthacene, TCNE/pentacene and the reaction mechanism of TCNE/anthracene

3.2: General synthetic procedure for TCNE/polyaromatic Adduct

DA adducts of TCNE/anthracene and TCNE/phencyclone were prepared following literature procedures.[20,21] The preparation of TCNE/naphthacene adduct was also straightforward (details in the experimental section). Pentacene is deep blue crystalline substance which is sparingly soluble in organic solvents. Therefore, preparing TCNE/pentacene adduct was challenging due to low solubility of pentacene. During the reaction with TCNE and Pentacene we get two adducts. The percentage of the side product (5, 14) can be decreased if we carry the reaction in relatively high temperature adduct.

Figure 13 Isomer of TCNE/pentacene adduct

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We found that heating the reaction mixture at about 100 ^{o}C yielded exclusively the (6, 13) adduct showed in Figure 1. Therefore, although TCNE reacts with pentacene extremely fast at room temperature, the reaction was conducted at 100°C. Pure (6,13) adduct was obtained with 72% yield after purification.

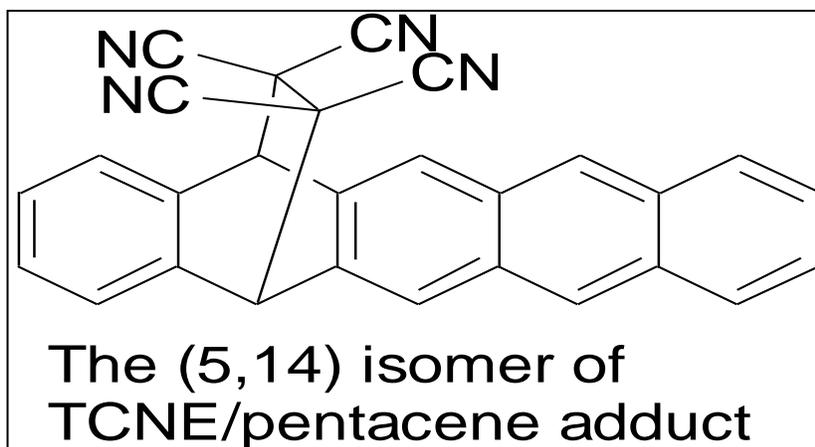One challenge of analyzing PrDA reactions of the TCNE adducts is that TCNE reacts with these polyaromatic dienes so fast that any PrDA products will immediately undergo DA reaction and change back to the DA adduct unless the product is stabilized or reacts with other reagents. To solve this problem, we added methanol to react with the TCNE which prevents the reverse reaction.[22]

3.3: General discussion on Photochemistry, quantum yield and chemical actinometer

In order to provide a detailed explanation of the feasibility of Photo-Retro DA reaction of TECNE/Polyaromatic compounds, it is very important to understand the basics of Photochemistry, quantum yield and chemical actinometer. Photochemistry is a field of chemistry in which chemical transformations are carried out by the emission or absorption of visible light or ultraviolet radiation. A molecule at its ground state (not excited) can absorb light or a quantum of light energy, or photon, and then transform to a higher-energy state, which is considered as the excited state of the molecule. This kind of excited molecule becomes much more reactive than a ground state molecule. It undergoes entirely different kind of reactions compared to the molecule at ground state. The following outcomes are possible when a molecule is being excited.

a) Excited molecule can emit the absorbed light and then returns to it's original ground sate position.

b) Instead of emitting light, excited molecule can undergo chemical changes.

In ground state chemical changes are described by chemical yield of the chemical reaction, while in excited state chemical changes are associated with a different parameter, which is Quantum Yield (Φ) of the reaction. Thus quantum yield (QY) can be defined as the number of events (i.e; photo induced transformations) divided by the number of absorbed photons for a specific chemical reaction. In a simple way, it is possible to express quantum yield (Φ) in the following ways

Φ = number of molecules undergoing that process of chemical change/number of quanta or photon absorbed

Φ = rate of the process/rate of absorption

Quantum yields follows the range of 0 to 1 or higher; if QY is smaller than 0.01, then the conversion/chemical change is believed to be very slow. On contrary for photo initiated chain reactions the QY can be as high as 1. Thus from these examples it is very clear that QY is directly associated with the chemical transformation of the photo induced molecule. Now it is imperative to determine the QY of a specific light-induced chemical transformation. A standard chemical procedure used since the 1920s is chemical actinometry[27]. This consists a chemical system of a fluid or a gas or a solid (in a microheterogenious misture). This chemical composition can undergo a light induced reaction at a certain wave length, (λ) for which QY (Φ) at λ is perfectly known. The following mathematical relationship was referenced from Ref-27.

The rate of change of an actinometric compound (Act) is the product of the incident light intensity (I_0), the quantum yield Φ, and the fraction of light absorbed by the compound (f) [27].

$$\overline{}$$ **(1)**

Based on the above equation we used a slightly different but fundamentally same mathematical expression to calculate the QY of a chemical reaction.

$$\Delta A(r) \, V(r) \, / \, F(r) \, e(r)l(r)t(r) \; = \; \Delta A(s) \, V(s) \; / \; F(s) \, e(s)l(s)t(s) \tag{2}$$

r = reference, s = sample, ΔA= absolute value of absorption difference, F = Quantum yield, e= extinction coefficient, l = optical length and t = time of irradiation.

In this kind of calculations, the concentration of the actinometric compound and the pathway of the photo-exposure cell must be quite high to make kinetics of the reaction approx. zero order. If we can achieve a zero order reaction during the Photo-Irradiation, then it can be assumed that the reaction is not dependent on the concentration of reactant. In these projects for all the measurements of QY we used uridine as the chemical actinometer—which is hydrated under UV irradiation with a known quantum yield of 0.018 at 254 nm.[23,24] The stepwise Photochemical reaction procedure for this experiments are mentioned bellow.

a)Millimoler solution of TCNE/DA adducts were prepared in a mixture of acetonitrile and methanol, b) Solutions were degassed by thaw-freeze method before irradiation, c) Millimoler solution of DA adducts in a quartz tube were irradiated at 254 nm using 8 W Spectroline ENF 280C lamp, d) Cautiously controlled reaction time-so that less than 5% of starting material reacted, which allows to lower the error, e) absorption was about "2", which meets total

absorption requirement for chemical actinometry—which shows that the rate of the chemical change upon UV irradiation is not dependent on concentration of TCNE/DA adduct.

Uridine   Photohydrate of uridine
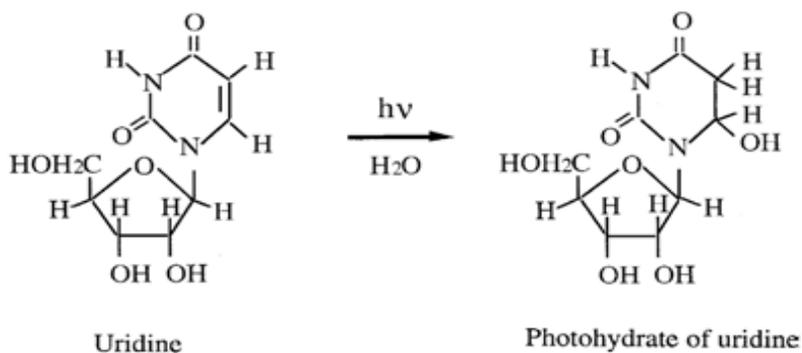
shows maximum absoption at 260nm

Figure 14 Uridine, chemical change of Uridine upon UV absorption

Polyaromatic analogs show absorption beyond 280nm. Pottasium Ferrioxalate,potassiumiodide, uridine actinometers show maximum absorption of proton at UV-C. Among these UV-C active actinometrs Uridine is characterised by a QY that is quite low relative to other actinometer. QY of our reaction was low-thus we chose Uridine In this experiment we used a mixture of acetonitrile and methanol solution. Acetonitrile is good solvent for polyaromatics. Addition of methanol was absolutely imperative to avoid the possibility of formation of DA adduct (forward reaction) after a successful PrDA reaction of TCNE/DA adduct.
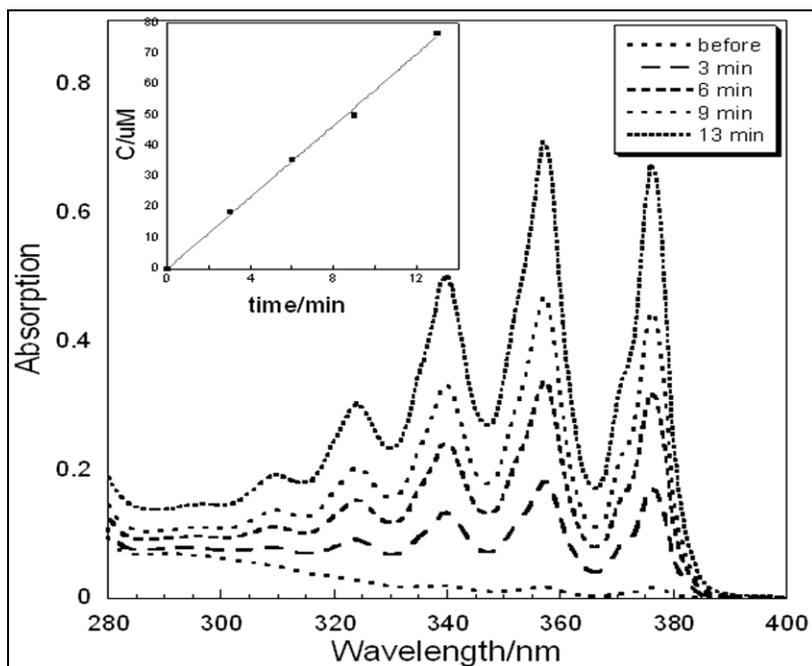
Figure 15 UV absorption change during photo irradiation of TCNE/anthracene adduct

A linear relationship (inserted picture at Figure-15) confirms that the PrDA reaction follow a zero order reaction. This was absolutely necessary "total absorption" condition in the early stage of the photo-transformation. In this period the quantum yield were calculated with chemical actinometry.

3.4: Structure based comparison with Quantum yields of the different PrDA reaction of the adduct

Quantum yields (QY) of PrDA reaction of TCNE/anthracene, TCNE/napthacene, TCNE/pentacene DA adducts were measured. From TCNE/anthracene adduct we received quantum yield of a 0.021 (Figure 2). In this case we observed that the PrDA reaction was

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happening very fast and dark condition was not required to fulfill this reaction. The QY of TCNE/ napthacene adduct was found (Φ =0.185) and it clearly shows that QY of PrDA reaction of TCNE/ napthacene DA adduct is an magnitude higher than QY of TCNE/anthracene adduct. Interestingly QY of TCNE/pentacene (Φ=0.019) adduct was almost same as TCNE/anthracene adduct. The trend of the quantum yields follows as------ (TCNE/naphthacene > TCNE/anthracene $\geq$ TCNE/pentacene). This trend of QY can be successfully explained by the following two theoretical assumptions.

a) Stability of the charge separated intermediates (Figure 12) of PrDA reaction of all three TCNE/polyaromatic DA adducts.

b) Stability of the TCNE/polyaromatic DA adducts.

During the PrDA reaction we can obtain a charge separated intermediate state as shown as Figure2. The stability of this charge separated intermediate state has definite influence of outcome of the product. The higher the stability, the greater the extent of PrDA reaction. We are considering the resonance effect to determine the relative stability order of these intermediates. The number of resonating structures of charge separated intermediates for TCNE/pentacene, TCNE/naphthacene, TCNE/anthracene are 11, 9 and 7 respectively. Thus, the stability order of the charge separated intermediate states of this TCNE/DA adducts is TCNE/anthracene < TCNE/naphthacene < TCNE/pentacene. Based on this observation, the extent of PrDA reaction (QY of PrDA reaction) should follow the following order.

TCNE/anthracene < TCNE/naphthacene < TCNE/pentacene. But in practice, we are getting a different picture. To explain the reality of our observation we employed a different approach. The stability of DA adducts were determined in order to support our observation of QY of PrDA

reaction of the three different TCNE/polyaromatic adducts. The difference of the resonance energy of the DA adduct (i.e; starting material) and the polyaromatic compound (i.e; product) shall be useful in determining the relative stability of these DA adducts. In this case, we can ignore the resonance energy of TCNE, as all the three DA adducts have TCNE in common. Finally, the content of resonance energy of a particular DA adduct is equal to the sum of energy content by aromatic moieties. Resonance energy, of TCNE/napthacene adduct is very close to the resonance energy of a benzene plus that of a napthacene molecule. Based on the data's--- reported by Herdon and Hosoya[25], we were able to determine (polyaromatic product-DA adduct) the resonance energy of different three TCNE/DA adduct. We got resonace energies of three DA adducts (.-0.11, -0.37, and -0.66 ev) for TCNE/anthracene, TCNE/naphthacene, TCNE/pentacene respectively. As, the stability of DA adducts influences the PrDA reaction, we found that, TCNE/anthracene adduct can undergo PrDA reaction at room temperature while, the other two required heating ($\sim 100^0$C). Thus the order of stability of DA adduct can maintain the following trend.

TCNE/anthracene < TCNE/naphthacene < TCNE/pentacene

These two theoretical assumptions follow the same trend, but have opposite effect in PrDA reaction. For this reason, TCNE/napthacene adduct generated highest QY during PrDA reaction of TCNE/napthacene Da adduct. From the above observations, we can also conclude that these reactions (PrDA) are not photo-thermal reactions.

CHAPTER FOUR: EXPERIMENTAL SECTION

4.1: An overview

All starting materials for preparing the DA adducts were purchased without further purification. HPLC grade solvents were used without further purification except degassing. TCNE/anthracene and TCNE/phencyclone adducts were synthesized following literature procedures.[20,21]

4.2: Photochemical Conditions

Millimolar solutions of the DA adduct in a quartz tube were irradiated under 254 nm UV light using a 8 W Spectroline ENF 280C lamp. Quantum yields were measured by chemical actinometry using uridine as the chemical actinometer.[23,24] For each solution, the absorption at 254 nm was about 3, which meets the "total absorption" requirement of chemical actinometry. All solutions were degassed by freeze-thaw method before irradiation. The reaction time was controlled so that about 5% of starting material reacted, which lowers the error caused by the absorption of the product. The concentrations of the products were analyzed by the long-wavelength absorption of the polyaromatic products. For every compound, multiple measurements were conducted to obtain a reliable value.

## 4.3: Synthesis of TCNE/naphthacene adduct

Naphthacene (150 mg, 0.69 mmol) and 10 mL of toluene were added to a round bottom flask equipped with a magnetic stir bar. The flask was sealed and purged with nitrogen then heated to 60°C. Tetracyanoethylene (104 mg, 0.8 mmol) was added to 6 mL of toluene and stirred leaving a small fraction of undissolved solid left. The liquid portion of this solution was extracted and

injected dropwise into the the hot naphthacene solution. The resulting mixture was maintained at 60°C with stirring for 30 minutes, then cooled to 0°C and vacuum filtered to obtain a white solid. (108 mg, 44% Yield) ^{1}H NMR. (CDCl$_3$, 500MHz): δ/ppm = 8.05 (s,2H), 7.91 (q, 2H, J=3.31, 6.18), 7.63 (m, 4H), 7.49 (q, 2H, J=3.25, 5.46), 5.17 (s, 2H).

4.4: Synthesis of TCNE/pentacene adduct

A solution of TCNE (82.7 mg ,0 .64 m mol) in degassed Toluene (8ml) was added to a stirring mixture of Pentacene (150 mg , 0.53 m mol) in degassed toluene (12 ml) in inert atmosphere . The mixture was degassed again by freeze-thaw method then heated for 3 hrs at 100 ^{0}C. The reaction mixture was cooled to rt and the precipitate was collected by filtration. The precipitate was dissolved in acetonitrile again and the insoluble unreacted pentacene was removed by filtration. The filtrate was rot. vap. and the remaining product was collected . (160 mg , 72% yield) 1H NMR (500 MHz , CDCl3): δ/ppm = 8.07(s , 4 H), 7.91 (dd , J1=3.3 Hz , J2 = 6.1 Hz , 4 H) , 7.60 (dd , J1 = 3.2 Hz , J2=6.3 Hz , 4 H) , 5.30 (s , 2 H).

APPENDIX A: NMR DATA OF ANTHRACENE AND TCNE
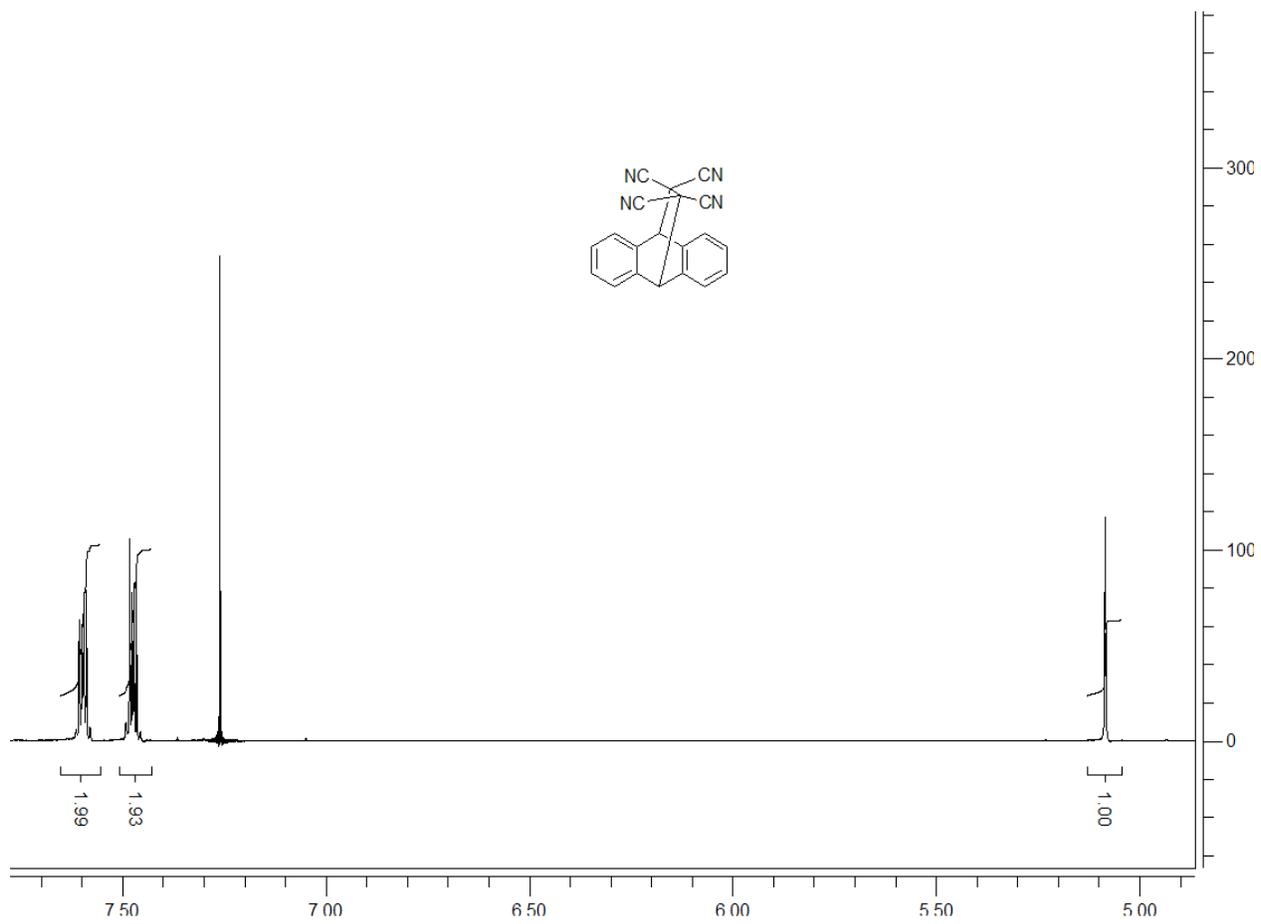
APPENDIX B: NMR DATA OF NAPTHACENE TCNE ADDUCT
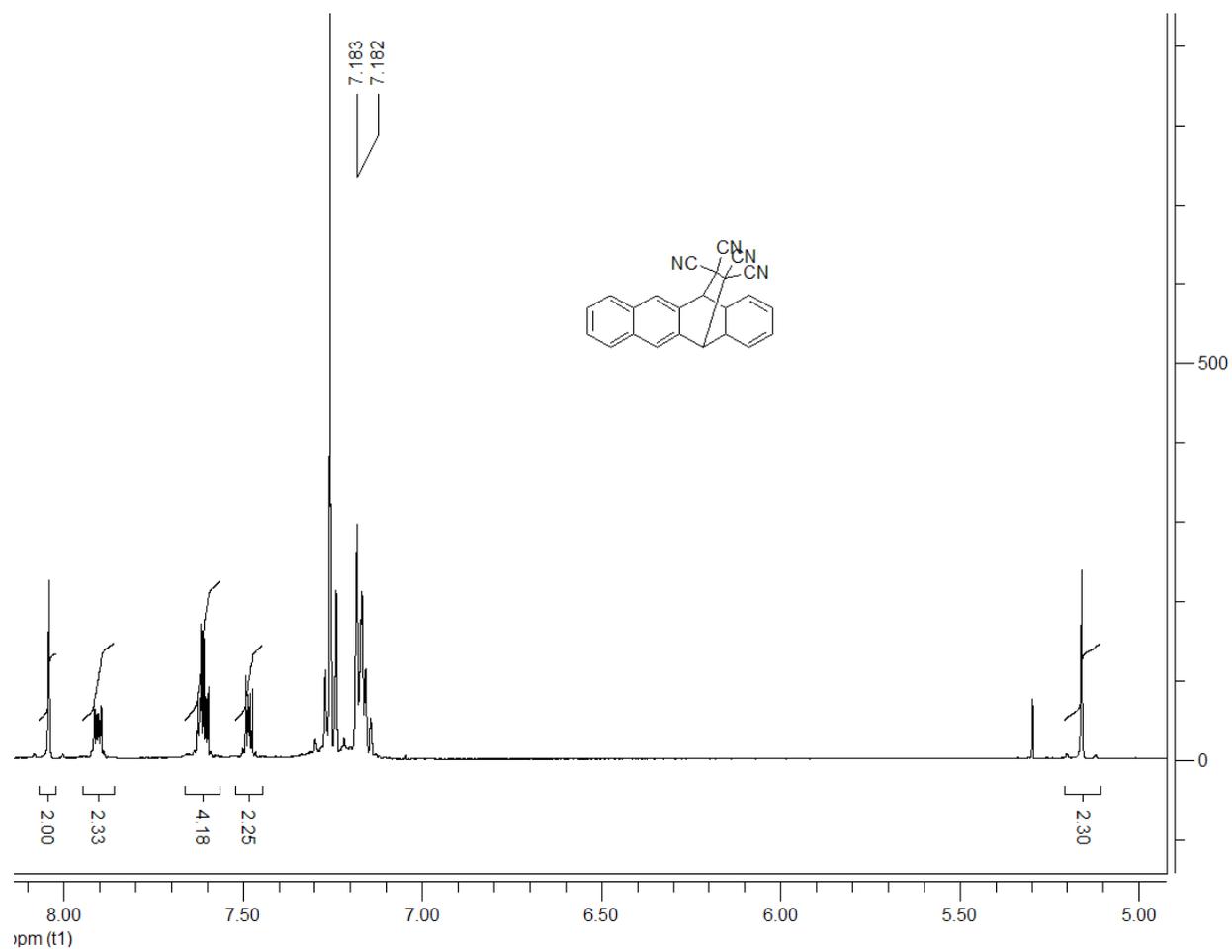
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