Red-Shifted Absorption Spectra of Anthracene Dye in Different Solvents

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Abstract
The absorption spectra of anthracene were studied and measured in the non-polar solvent cyclohexane and in the polar solvent methanol at two concentrations [10^{-4} M] and [10^{-5} M]. The results showed a small shift of the absorption spectra of anthracene towards longer wavelengths (red shift) in the non-polar solvent (cyclohexane). These measurements were made at room temperature (20°C).

Keywords: Spectroscopy; UV-visible spectrophotometry; Anthracene dye; Cyclohexane solvent
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1. Introduction

Anthracene is an aromatic organic compound which have rings groups in their structure. The benzene ring is the simplest types of aromatic compounds consisting of six carbon atoms and six hydrogen atoms [1,2]. These are polycyclic aromatic hydrocarbons and also considered organic semiconductors. In last few years organic semiconductors have attracted an increasing technologic interest which is accompanied by a significant progress in fundamental research related to these materials. Organic semiconductors are carbon based compounds that show semiconducting properties. All kinds of optoelectronic devices including organic light emitting diodes (OLEDs), organic solar cells, and organic field effect transistors, memories, and sensors, have been made using this class of semiconductors [3-7].

Anthracene dyes are a class of dyes that incorporate this anthracene skeleton as their primary structural unit [8]. The actual color and specific properties of an anthracene dye are determined by the presence and position of various auxochromic (color-enhancing) and chromophoric (color-imparting) substituent groups attached to the anthracene core [9]. These substituents can include groups like amino ($-NH_2$), hydroxyl (-OH), nitro ($-NO_2$), or sulfonic acid ($-SO_3H$) groups, which modify the electron distribution within the molecule and thus its interaction with light [10]. Figure (1) shows the chemical structure of Anthracene ($C_{14}H_{10}$).

Anthracene dyes in non-polar cyclohexane typically exhibit well-defined vibronic structures in their absorption and fluorescence spectra, characteristic of a rigid, unperturbed chromophore [11,12]. The Stokes shift is generally modest, and fluorescence quantum yields can be high due to minimal solvent-induced non-radiative decay. In contrast, when dissolved in polar, protic methanol, the spectroscopic behavior changes [13]. The absorption spectrum might show slight shifts, but the emission spectrum often displays a significant bathochromic (red) shift [14]. This solvatochromism arises from the stabilization of the more polar excited state by methanol [15,16]. Hydrogen bonding between methanol and the dye can also promote non-radiative relaxation pathways, potentially leading to a decrease in fluorescence quantum yield and a broadening of the spectral bands [17,18].

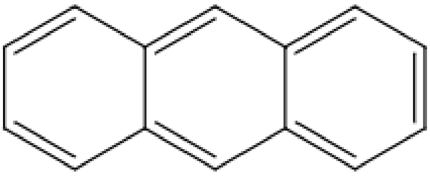

Fig. (1) Chemical composition of Anthracene ($C_{14}H_{10}$)

This work aims to study of the effect of solvent on the absorption spectra of anthracene compound dye.

2. Experimental Part:

The 99.5% pure anthracene (AN) compound dissolved in the solvents (cyclohexane 99% and methanol 99.5%). The AN was prepared with concentrations [10^{-4}M] and [10^{-5}M] at room temperature. The solutions were prepared using the following relationship:

$$W = \frac{[M]\times V\times M.W.}{1000} \qquad (1)$$

where W is the weight of material in gram, M.W. is the molecular weight gm/mol, [M] is the molar concentration (mol/L), and Vis the volume of solvent used to dissolve the material in ml.

The prepared solutions were diluted according to the following equation [19]:

$$[M]_1V_1 = [M]_2V_2 \qquad (2)$$

where $[M]_1$ is the primary concentration, $[M]_2$ is the new concentration, V_1 is the volume before dilution, and V_2 is the volume after dilution

The absorption spectra was recorded in the spectral range of 190-900 nm by a CARY 100 Conc. UV-Visible dual-beam spectrophotometer.

3. Results and Discussion

The spectrum of (AN) consist of five peaks located at different wavelengths as shown in table (1). Figure (2) displays the UV-Vis absorption spectra of anthracene, revealing its electronic transition properties. The distinct peaks observed, particularly in cyclohexane (red line), represent vibronic transitions – simultaneous changes in electronic and vibrational energy levels, governed by the Franck-Condon principle. The energy of absorbed photons corresponds to the $S_0 \rightarrow S_1$ electronic excitation.

Comparing the spectra, the shift between cyclohexane (non-polar) and methanol (polar) is minimal for absorption. This indicates that the energy difference between the ground and the lowest singlet excited state of unsubstituted anthracene is not dramatically perturbed by this change in solvent polarity. The selected text highlights that substituents create "anthracene dyes" by modifying electron distribution. While this figure likely shows unsubstituted anthracene, the introduction of such auxochromic or chromophoric groups would significantly alter the energy levels of the π-electron system, leading to more substantial shifts in these absorption bands and thus different perceived colors, due to their electron-donating or withdrawing effects.

Table (1) The peak locations for the absorption spectra of AN in different solutions at concentrations of [10^{-4} M] and [10^{-5} M]

Concentrations[10^{-4}M]	Bands				
Solvent					
Cyclohexane	311	325	341	357	376
Methanol	310	324	340	356	375
Concentrations[10^{-5}M]	**Bands**				
Solvent					
Cyclohexane	311	325	341	357	376
Methanol	310	324	340	356	375

From Fig. (3), it can be noticed that the absorbance increases with increasing of the molecular concentration of solution. According to Beer-Lambert law, the increasing in the molecular concentration of solution leads to increases in the number of molecular in the solution and this lead to increases in the absorbance, which agrees with [20,21]. Also, on the other hand, noticed a small shifted for absorption spectra toward the long wavelengths (red shift) in non-polar solvent (cyclohexane), because the viscosity of cyclohexane is greater of the viscosity methanol.

This figure presents the UV-visible absorption spectra of anthracene at a lower concentration (10^{-5} M), again in cyclohexane (red) and methanol (black). The persistence of the well-defined vibronic structure was noted, which is an indicative of quantized electronic transitions coupled with vibrational modes. The energy of absorbed photons promotes electrons from the S_0 ground state to the S_1 excited state.

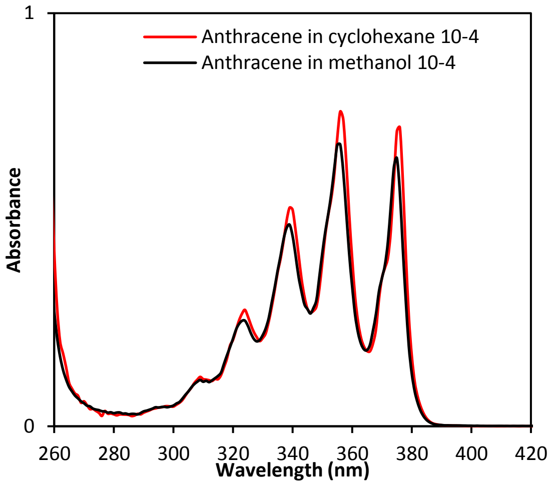

Fig. (2) Absorption spectra of AN concentration of [10^{-4} M] dissolved in cyclohexane (red line) and in methanol (blue line)

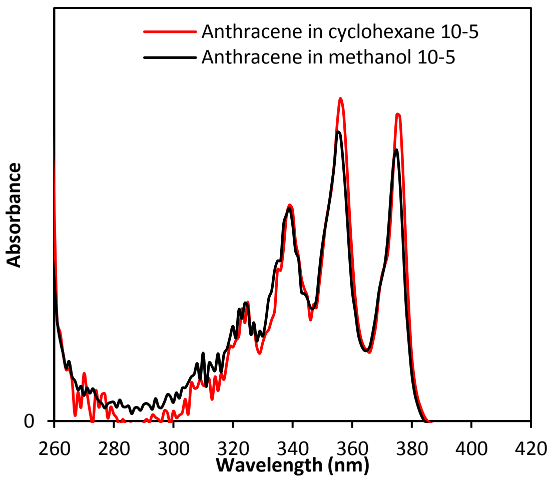

Fig. (3) Absorption spectra of AN concentration of [10^{-5} M] dissolved in cyclohexane (red line) and in methanol (blue line)

The key observation here is that even at this lower concentration, the absorption peak positions show minimal solvatochromic shift between the non-polar cyclohexane and polar methanol. This suggests the dipole moment change upon excitation for *unsubstituted* anthracene is small, so solvent polarity has a limited effect on the S_0-S_1 energy gap. The increased noise, particularly below 320 nm, is a typical consequence of reduced analyte concentration, impacting the signal-to-noise ratio of the spectrophotometer.

The electronic transitions from the zero-point vibrational level of electronic ground state (S_0) to the vibrational levels of electronic excited state (S_1), which corresponds to the (0–0), (0-1), (0-2), (0-3), (0-4) electronic transition.

The molecular concentration of solution defects the intensity of Anthracene absorption spectra, the molar extinction coefficient for solute molecule depends on wavelength of incident photon on the sample and the type of solvent and this is agreement with [8].

When molecule absorbed at different concentration of light and the effects of the solvent dielectric constant its clear and this is agreement with [9]; its transition to excited electronic state changes the electronic distribution of the solute molecule and a change in the value of the electric dipole moment of the molecule. It is also known as the relaxation processes of solute molecules.

4. Conclusions

The study shows the absorption for molecules anthracene that the value of the spectrum intensity clearly affected with concentrations of solutions .The higher concentration corresponds of solutions with greater value absorption spectrum. The results showed a small shifted the absorption spectra of anthracene toward the long wavelength (red shift) in non-polar solvent (cyclohexane), because the viscosity of cyclohexane is greater of the viscosity methanol.

References

[1] F.A. Carey, **"Organic Chemistry"**, 4th ed., McGraw-Hill (NY, 2000).
[2] G.D. Scholes, "Long-Range Resonance Energy Transfer in Molecular Systems", Annual Rev. Phys. Chem., 54 (2003) 57-87.
[3] D.L. Dexter, "A Theory of Sensitized Luminescence in Solids", J. Chem. Phys., 21(5) (1953) p. 836.
[4] S.T. Roberts et al., J. Phys. Chem. Lett., 2 (2011) 48-54.
[5] A.A. Anber et al., "Spectroscopic Study of Chromium-Doped Silicon Nitride Nanostructures Prepared by DC Reactive Magnetron Sputtering", Iraqi J. Appl. Phys., 17(2) (2021) 11-14.
[6] J.C. Johnson, A.J. Nozik, and J. Michel, "High Triplet Yield from Singlet Fission in a Thin Film of 1,3-Diphenylisobenzofuran", J. Am. Chem. Soc., 132(46) (2010) 16302-16303.
[7] C.L. Lee et al., "Triplet Exciton and Polaron Dynamics in Phosphorescent Dye Blended Polymer Photovoltaic Devices", Adv. Funct. Mater., 20(17) (2010) 2945-2950.
[8] X. Zhou, H. Zhang, and Y. Liu, "Cyclodextrin supramolecular assembly confined luminescent materials", Chem. Sci., 15(44) (2024) 18259-18271.
[9] Z.H. Zaidan et al., "Effect of structural phase on photocatalytic activity of titanium dioxide nanoparticles", Iraqi J. Appl. Phys., 19(3A) (2023) 55-58.
[10] F. Jesus et al., "A review on polycyclic aromatic hydrocarbons distribution in freshwater ecosystems and their toxicity to benthic fauna", Sci. Total Enviro., 820 (2022) 153282.
[11] X. Li et al., "Photoswitches and photochemical reactions for optically controlled phase transition and energy storage", Chem, 9(9) (2023) 2378-2389.
[12] D.C.C. Silva, J.C. Marques, and A.M.M. Gonçalves, "Polycyclic aromatic hydrocarbons in commercial marine bivalves: Abundance, main impacts of single and combined exposure and potential impacts for human health", Marine Pollut. Bull., 209(B) (2024) 117295.
[13] X. Wu and C. Barner-Kowollik, "Fluorescence-readout as a powerful macromolecular characterisation tool", Chem. Sci., 14(45) (2023) 12815-12849.
[14] S. Cortés-Bautista, C. Molins-Legua, and P. Campíns-Falcó, "Miniaturized liquid chromatography in environmental analysis. A review", J. Chromatog. A, 1730 (2024) 465101.
[15] M. Koshimizu, "Fundamental processes and recent development of organic scintillators", J. Lumin., 278 (2025) 121008.
[16] T.S. Ahn et al., "Self-absorption correction for solid-state photoluminescence quantum yields obtained from integrating sphere measurements", Rev. Sci. Instrum., 78 (2007) 086105.
[17] S.A. Barghouthi, J. Perrault, and L. H. Holmes, "Effect of Solvents on the Fluorescence Emission Spectra of 1-Anilino-8-Naphthalene Sulfonic Acid: A Physical Chemistry Experiment", Springer-Verlag, (NY, 1998), Vol. 3, No. 5, pp. 1-10.
[18] M.K. Khalaf et al., "Effect of Adding Nitrogen to the Gas Mixture on Plasma Characteristics of a Closed-Field Unbalanced DC Magnetron Sputtering System", Iraqi J. Appl. Phys., 10(1) (2014) 27-31.
[19] S.M. Sundaram et al., "Effect of anthracene doping on potassium hydrogen phthalate crystals", J. Therm. Anal. Calorim., 100(3) (2010) 821-826.
[20] F. Würthner and M. Hariharan, "Control of photoluminescence properties by tailored supramolecular matrices", Trends in Chem., 7(5) (2025) 208-224.
[21] S.J. Strickler and R.A. Berg, "Relationship between absorption intensity and fluorescence life-time of molecules", J. Chem. Phys., 37 (192) 814-822.