

Characterization of Phenanthrene Single Crystals

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Abstract

Single crystals of phenanthrene were successfully grown from melt using Bridgeman Crystal Growth System Type 365. The starting material was purified by sublimation and zone refining techniques in specially designed crystal growth tubes. Phenanthrene single crystals grow with the plane of maximum growth corresponding to the ab-crystallographic plane, and cleave readily in this plane. The optical absorption spectra of phenanthrene single crystals and phenanthrene crystals dissolved in benzene, alcohol and acetone solutions were studied in the wavelength range (200 - 400 nm). The optical excitations i.e., $\pi - \pi^*$ transitions, are attributed to the weak and strong optical absorption in such crystals, and crystals dissolved in different solutions. The region of strong absorption shows three absorption bands 1C_b , 1B and 1L_a while 1L_b band refers to weak absorption region. The optical bandgap energy of these crystals was found to be 3.16 eV and for crystals dissolved in different solutions was found to vary from 3.72 eV to 3.78 eV and is in agreement with other published data.

1. Introduction

Spectrophotometric studies of organic single crystals provide useful information regarding the band structure, energy bandgap and the internal electronic transitions. Various investigators [1-3] have published data on optical properties and excited state dynamics of different kinds of organic single crystals. The optical absorption and photoconductivity studies of organic single crystals [4-7] and mixed organic crystals [8] have also been reported. Phenanthrene [$C_{14}H_{10}$] is an isomer of anthracene and crystallizes in the same monoclinic structure C_{2h}^5 as does anthracene. Both consist of three benzene rings

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but anthracene in a linear geometry whereas phenanthrene in an angular geometry [7,8]. The structural similarities and differences provide a clue to understand the electronic behaviour of phenanthrene crystals in comparison with anthracene.

The aim of present work is, therefore, to study the optical absorption spectra in the wavelength range (200 - 400 nm) for phenanthrene single crystals and crystals dissolved in different solutions in order to understand which type of internal electronic transitions are responsible for the observed peaks in their optical absorption spectra. Furthermore, the optical absorption spectra of phenanthrene are also compared with the already published data [9-12]. Measurements of optical bandgap energy, carrier mobility and activation energy for electrical conduction in these crystals is also presented.

2. Experimental

Single crystals of phenanthrene were grown from the melt using the Bridgeman Crystal Growth System Type 365. The starting material, i.e., synthetic phenanthrene was obtained from the British Drug House Chemicals Limited, U.K. (purity ~ 1 ppm) and further purified by sublimation and zone refining techniques in specially designed crystal growth tubes [4,5,7,8]. A small quantity (approx. 0.001mg) of phenanthrene crystals was dissolved in 20 ml of benzene, alcohol, or acetone to make solutions. Optical absorption spectra of these solutions and phenanthrene single crystals were recorded in the ultra-violet wavelength range (i.e. 200-400 nm) using Hitachi U-2000 Spectrophotometer.

The dc conductivity measurements of phenanthrene single crystal having dimensions $4.35 \text{ mm} \times 4.1 \text{ mm} \times 1.93 \text{ mm}$ were performed as a function of temperature at a fixed bias field by the two probe technique. Keithley 610C Electrometer (sensitivity $\sim 10^{-14} \text{ A}$) was used for current measurements and Ortec dc regulated power supply for applying the fixed bias field.

3. Results and Discussion

Phenanthrene single crystals were transparent and free from striations. The unit cell of phenanthrene crystal is monoclinic with dimensions ($a = 8.57 \text{ \AA}$, $b = 6.11 \text{ \AA}$, $c = 9.47 \text{ \AA}$) and angle β is 97.5° [13]. Phenanthrene single crystals grow with a plane of maximum growth corresponding to ab-crystallographic plane and cleave readily in this plane. It is experimentally found that if the angle of capillary to the vessel axis is $< 45^\circ$, ab-plane will grow parallel to the vessel axis, but if the angle is $> 45^\circ$, this plane will grow perpendicular to the vessel axis [4, 5, 14 - 16]. For the growth of phenanthrene single crystals, ab-cleavage planes were horizontal (i.e. perpendicular to vessel axis).

The optical absorption spectra of a typical phenanthrene single crystal and phenanthrene crystals dissolved in different solutions are shown in Fig. 1. It is obvious from Fig. 1 that the spectral response of the single crystal is not sufficiently sharp and all the peaks in the spectrum cannot be distinguished easily. However, absorption spectra for the solutions are relatively sharp and absorption peaks can easily be distinguished. Table 1 shows a comparison of absorption peaks observed in the present investigations with optical absorption peaks of phenanthrene in ethanol [11] and cyclohexane [12] solutions.

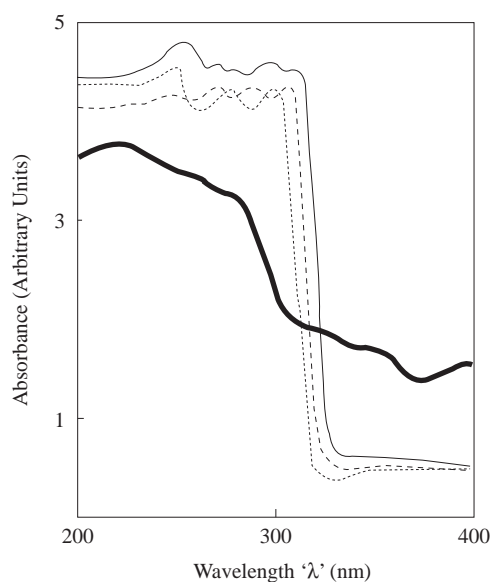


Figure 1. Optical absorption spectra for a typical phenanthrene single crystal (—) and phenanthrene crystals dissolved in Alcohol (.....), Benzene (- - -) and Acetone (- . -) solutions.

Table 1. Comparison of the Optical Absorption Data of Phenanthrene Single Crystal and Crystals Dissolved in Different Solutions.

| Previous Work (Literature) | | Present Work | | | | |
|---|---|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|--------------------------------|
| Ethanol λ_{\max} (nm) [Ref. 11] | Cyclohexane λ_{\max} (nm) [Ref. 12] | Alcohol λ_{\max} (nm) | Benzene λ_{\max} (nm) | Acetone λ_{\max} (nm) | Crystal λ_{\max} (nm) | Optical Absorption Band. |
| — | 219 | — | — | — | 220 | 1C_b |
| 223 | 223 | — | — | — | — | |
| 242 | 245 | — | — | — | — | 1B |
| 251 | 252 | 250 | 250 | 251 | 252 | |
| 274 | 274 | 275 | 272 | 270 | — | 1L_a |
| 281 | 282 | — | — | 281 | 280 | |
| — | 289 | 297 | 288 | 297 | — | |
| 293 | 292 | — | 306 | 308 | — | |
| 309 | 309 | — | — | — | — | 1L_b |
| 314 | 316 | — | — | — | — | |
| 323 | 323 | — | — | — | — | |
| 330 | 330 | — | — | — | 330 | |
| 337 | 338 | — | — | — | — | |
| 345 | 346 | 350 | 350 | — | 350 | |

The region of weak optical absorption i.e. 309-400 nm is attributed to $\pi-\pi^*$ electronic transition corresponding to 1L_b absorption band. This 1L_b band is found hidden under the strong 1L_a absorption band of anthracene [9], but is clearly visible in phenanthrene crystals. The molecular vibrations cause the splitting of absorption peaks [Table 1] for $\lambda > 308$ nm [4, 8, 14]. In this region a weak exciton - phonon interaction was also observed by K. Tomioka et. al. [10]. In the region of strong optical absorption i.e. 210-308 nm, the absorption peak at 220 nm is observed for single crystal [Table 1] and is due to $\pi-\pi^*$ excitation which corresponds to 1C_b band. This band is observed because of a transition that is forbidden in compounds with a center of symmetry e.g. anthracene etc. but occurs near 219 nm for compounds lacking this symmetry element, e.g. chrycene, phenanthrene etc. [9]. The optical absorbance peak at 250 nm observed in single crystal specimen and for crystals dissolved in alcohol and acetone solutions is also caused by $\pi-\pi^*$ transition corresponding to 1B absorption band similar to a peak observed in anthracene at about the same wavelength [9]. Optical absorption peaks in the region 270 - 308 nm can be correlated to 1L_a band and are also due to $\pi-\pi^*$ excitations as observed in anthracene and their splitting is due to molecular vibrations [9]. The absorption peaks in this region have been shifted towards longer wavelengths. This can be attributed to the nature of different solvents and/or to any residual impurity [7,17]. The photo-carrier pair generation in phenanthrene single crystal illuminated with monochromatic radiation takes place for $\lambda > 320$ nm [7]. Photo - current in this region is correlated with $\pi-\pi^*$ transition caused by weak optical absorption [7]. The optical bandgap energy, E_{opt} , for phenanthrene single crystal and crystals dissolved in different solutions can be calculated [18] by extrapolating the plots of $\alpha^{1/2}$ Vs photon energy ($\hbar\omega$) as illustrated in Fig. 2, where α denotes the optical absorption coefficient which is related to the absorbance A through a relation:

$$\alpha(\omega) = 2.303A/d,$$

where d is the thickness of the sample. Table 2 gives a comparison of experimentally determined values (from Fig. 2) of optical bandgap energy for phenanthrene single crystal and the crystals dissolved in different solutions. These values of optical bandgap energy are in agreement with other published work on different kinds of organic single crystals [4,19]. It is obvious from Table 2, that E_{opt} for the phenanthrene crystals dissolved in benzene, alcohol and acetone solutions is of the same order but slightly greater than E_{opt} for the phenanthrene single crystal.

Table 2. Comparison of the Optical Bandgap Energy ' E_{opt} ' for Phenanthrene Single Crystal and Crystals Dissolved in Different Solutions.

| Optical Bandgap Energy E_{opt} (eV) | | | |
|---------------------------------------|------------------|------------------|------------------|
| Phenanthrene Single Crystal | Benzene Solution | Alcohol Solution | Acetone Solution |
| 3.16 | 3.74 | 3.78 | 3.72 |

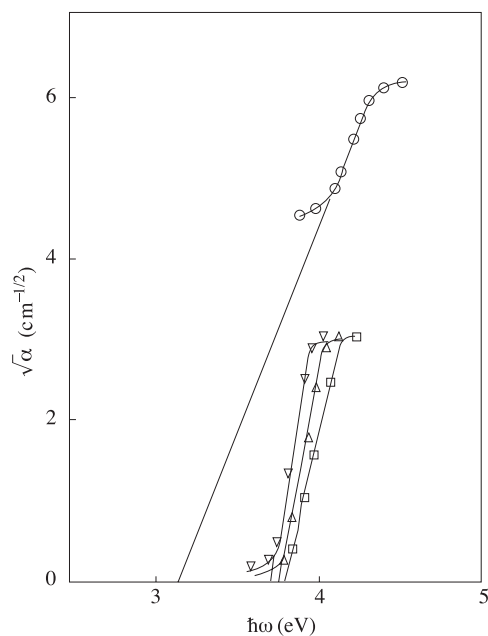


Figure 2. Plots of square root of optical absorption coefficient $\alpha^{1/2}$ versus photon energy $\hbar\omega$ for Phenanthrene single crystal (\circ) and phenanthrene crystals dissolved in Benzene (Δ), Alcohol (\square) and Acetone (∇) solutions.

The variation of log conductivity with $1000/T$ for phenanthrene single crystal is shown in Fig. 3. The electrical conductivity σ of the crystal follows the Arrhenius type equation:

$$\sigma = \sigma_o \exp.(-E_a/k_B T),$$

Where E_a is the activation energy for electrical conduction, k_B is the Boltzmann constant, T is the absolute temperature and σ_o is the pre-exponential factor given by $\sigma_o = eN_o\mu$; here, μ is the mobility of current carriers and N_o , the effective density of states in conducting levels of a crystal. Estimating value of N_o ($\sim 10^{21}$) from free molecular model [20] due to weak molecular interactions, the value of carrier mobility μ comes out to be $3.85 \times 10^{-11} \text{ cm}^2 \text{ volt}^{-1} \text{ s}^{-1}$ while E_a was found to be 0.375 eV (from Fig.3). These values of E_a and μ are in good agreement with those of other organic materials [20, 21].

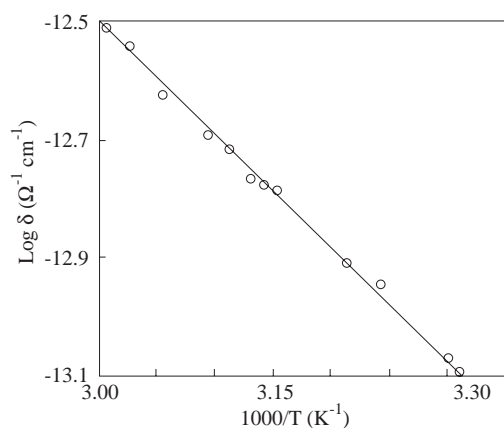


Figure 3. Plot of Log (conductivity ' σ ') versus $1000/T$ for phenanthrene single crystal.

4. Conclusions

1) Phenanthrene single crystals grow with a plane of maximum growth corresponding to ab-crystallographic plane and cleave readily in this plane. These crystals were transparent and free from striations.

2) The optical absorption spectra of phenanthrene single crystals are attributed to internal electronic transitions of $\pi - \pi^*$ type and are responsible for weak and strong optical excitations in such crystals.

3) The optical bandgap energy ' E_{opt} ' for the phenanthrene crystals dissolved in different solutions is of the same order but greater than that for phenanthrene single crystal.

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