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Conduction studies in anthraquinone derivatives. VI

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Contrary to the results of the early 1960s, it has been found that the anthraquinone (AQ) and its derivatives can be made photoconductive ($I_{Ph}/I_D \approx 10^3$) by substituting suitable donors in the periphery of the benzenoid rings. The conductivity of the AQ derivatives, generally speaking, are not as good as those of the charge transfer kind. The darkcurrent in the case of AQ derivatives ranges from 10^{-14}–10^{-12} for 9,10-AQ to 10^{-10}–10^{-8} for 1,4,5,8-tetra amino AQ. The AQs are n-type semiconductors with electrons being the majority charge carriers. In the present article, we describe the charge carrier generation and transport processes in three di-substituted AQ derivatives whose spectral properties have been well studied. The magnetic field effect has been observed for the first time in these compounds.

1. Introduction

Systematic investigation of the dark and photoconduction studies in dyes started in the late 1940s. Vartanyan [1] in Russia, Nelson [2] in the United States and Noddack [3] in Germany began independent studies in the above mentioned period. Vartanyan and Nelson obtained evidence of photoconduction in basic dyes only, but Noddack demonstrated that acidic and non-ionic dyes also exhibit this effect. Weigl [10] has correlated the photoresponse with the spectral properties of the dyes. Meier [11], Gutmann [12] and Pope and Swenberg [13] have reviewed the dark and photoconduction in different classes of dyes and the factors which affect this phenomena.

The anthraquinones are an important class of organic compounds which fall under the group of disperse dyes and have been studied extensively because of their structural relationship to the vat dyes and because they can promote photo-tendering of textiles [8]. Anthraquinone (AQ) derivatives are widely used as commercial dyes for both natural and synthetic fibres [9, 10]. Allen, Harwood and McKeller [11–13] have reported that a knowledge of the luminescence properties of the amino and hydroxy AQs make a valuable contribution to the understanding of the relationship between the structure and the light fastness [11–13].

AQs show photoconduction just as their corresponding hydrocarbons with out the carbonyl groups. The photoconductivity of AQs is about one order less than that of anthracene. This explains why AQs had been classified as non-photoconductive [14]. Moreover, carriers are produced both by n–π* excitation (410 nm) and by π–π* (250–300 nm). Because of the smaller extinction coefficients of the n–π* absorption in these cases, the carrier production in the sandwich cells take place in the entire sample, which means that no surface effects arise in the 410 nm action band of photoconduction. The observed asymmetry in the photocurrents in the sandwich cells on illumination in the 250–300 nm region when the positive or the negative electrode is illuminated respectively shows that the electrons are the majority charge carriers in contrast to anthracene [15].

In our earlier publication [16], we reported a possible relationship between the thermal activation energy of the dark conduction and the first excited singlet state energies of a series of substituted anthraquinones.

In the present communication, we report our results on the dark and photoconduction studies in three di-substituted AQs whose spectral properties are rather well studied [17–20]. It will therefore be interesting to study their photoconduction behaviour, since photoconduction is one of the competing phenomena associated with the excited state along with fluorescence, phosphorescence and radiationless degradation. The effect of various parameters such as the excitation wavelength, the intensity of radiation, the applied field and the temperature on the photoconduction behaviour has been studied with a view to understanding the nature of the charge carrier generation and the transport mechanism in the present series of compounds.

2. Experimental procedure

The compounds are commercially available and were purified by repeated recrystallization from purified ethanol. The compounds were further purified by

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column chromatography and vacuum sublimation. Surface-type raster cells having silver paste contacts with an electrode distance of 0.02 cm have been used for studying the electrical properties. The schematic diagram and the description of the experimental set-up has been given elsewhere [21, 22]. The raster cell has 35 gaps and the interelectrode distance was maintained at 0.02 cm and was prepared by photo-etching the aluminium coated (by vacuum sublimation at 1.3 $\times 10^{-2}$ Pa) on carefully cleaned transparent quartz slides. The dyes were sublimed at a vacuum better than 1.3×10^{-2} Pa on these gaps for the purpose of the conductivity measurements.

The samples were investigated in a vacuum of the order of 1.3×10^{-3}–1.3×10^{-4} Pa, in the temperature range 288–328 K, and in the potential range 0–150 volts. The dark and the photocurrents were registered with a picoammeter (model EA5600, Electronic Corporation of India). In addition, the rise and decay kinetics of the photocurrent have been measured by using the picoammeter in combination with a fast recorder (Rikin Denshi Model) having a chart speed of 0.5 s cm^{-1}. The light source consisted of a 450 W xenon arc lamp with a quartz tank containing water to cut-off the IR radiations from the lamp.

Out-gassing of the sample was carried out by cyclically heating and cooling the samples when kept under vacuum better than 1.3×10^{-4} Pa.

3. Results and discussion

3.1. Dark conduction

The dark current (I_D) observed in the three di-substituted AQs, namely, 1,4-diamino anthraquinone (1,4-DAAQ), 1,4-dimethylamino anthraquinone (1,4-DMAAQ) and 1,4-dihydroxy anthraquinone (1,4-DHAQ), shows a linear rise with the applied potential (field) and follows the relation,

$$I_D = aU^s \qquad (1)$$

where U is the applied field (V cm^{-1}), s is the voltage parameter and a is a constant. A plot of the logarithm of the applied field, $\log U$ (or $\log v$, where v is the applied potential in volts) gives s as the slope (Fig. 1). The value of s in these compounds is nearer to 1, showing a perfect ohmic behaviour. Therefore, an injection of charge carriers from the electrodes seems not to be favoured.

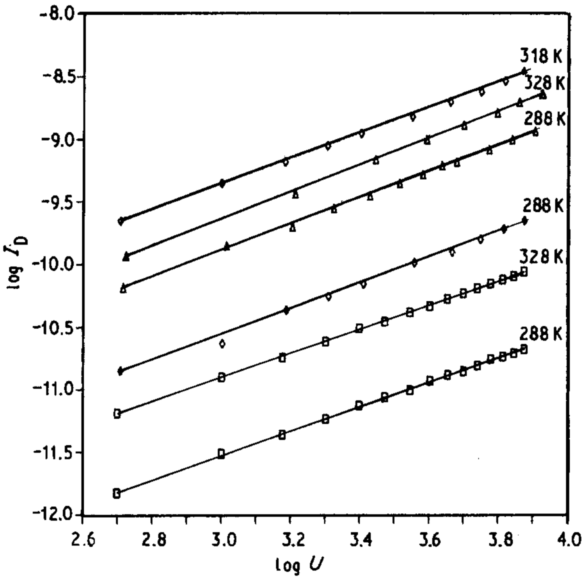

Figure 1 Plot of the logarithm of dark current versus the logarithm of the applied field in surface type raster cells (d = 0.02 cm) for (△) 1,4-DAAQ, (◇) 1,4-DMAAQ, and (□) 1,4-DHAQ. The temperatures at which they are measured are given.

The dark current of the AQs increases on transition from 1,4-DHAQ to 1,4-DAAQ and then to 1,4-DMAAQ (Table I). The enhanced dark conduction (compared to that of 9,10-AQ [16]) may be due to the substitution effect (the donating power increasing in the order 1,4-DHAQ < 1,4-DAAQ < 1,4-DMAAQ).

The thermal activation energy of dark conduction has been derived from the Arrhenius plot of the dark current by the Equation 2,

$$I_D = A \exp(-\Delta E_D/kT) \qquad (2)$$

where A is the pre-exponential constant, ΔE_D is the thermal activation energy of dark conduction, k is the Boltzmann constant and T is the temperature in Kelvin. For 1,4-DMAAQ, we observe a decrease (reversal) in the dark conductivity after 318 K. In this compound, which shows a reversal in the dark conduction, the thermal activation energy of dark conduction is higher (0.8366 eV), which means a deeper trap depth. In our earlier publication [16] we explained how the thermal activation energy can be correlated to the depth of traps in the energy gap for the compounds under discussion. Deep trap depths lead to a negative temperature coefficient of mobility

TABLE I The value of the voltage parameter for dark conduction, s, for the photoconduction, s', the thermal activation energy of dark conduction, ΔE_D, the thermal activation energy of photoconduction, ΔE_{Ph}, the intensity parameter, γ, observed in the compounds

Compounds	s value	ΔE_D (eV)	s' value	ΔE_{Ph} (eV)	γ values
1,4-DHAQ	0.653	0.2327	0.609 (0–50 V) 1.0585 (50–150 V)	0.3741	1.3–1.5
1,4-DAAQ	1.083	0.1235	1.012	0.2981	0.77–1.1 (Bet. 29–63%) 1.64–2.08 (Bet. 63–100%)
1,4-DMAAQ	1.006	0.83 (288–308 K) 0.47 (308–318 K) 0.49 (318–328 K)	1.005	0.2554	0.97–1.3 (Bet. 29–63%) 1.78–2.63 (Bet. 63–100%)

($-\mathrm{d}\mu/\mathrm{d}T$). This possibly accounts for the reversal of the dark current after a certain temperature.

On the other hand, the reversal in the dark current with increasing temperature and the negative activation energy after 318 K may be the result of a phase transition taking place in the compound. Similar effects have been observed in various organic solids [23–25]. The value of ΔE_D for the compounds under present discussion has been given in Table I.

3.2. Photoconduction

The surface conductivity measurements in the thin films of the compounds in the low field region (0–7.5 kV cm^{-1}) show that the photocurrent follows the relation,

$$I_{Ph} = a'U^{s'} \quad (3)$$

where s' is a power factor which is nearly equal to 1 for 1,4-DAAQ, showing a perfect ohmic behaviour. In the

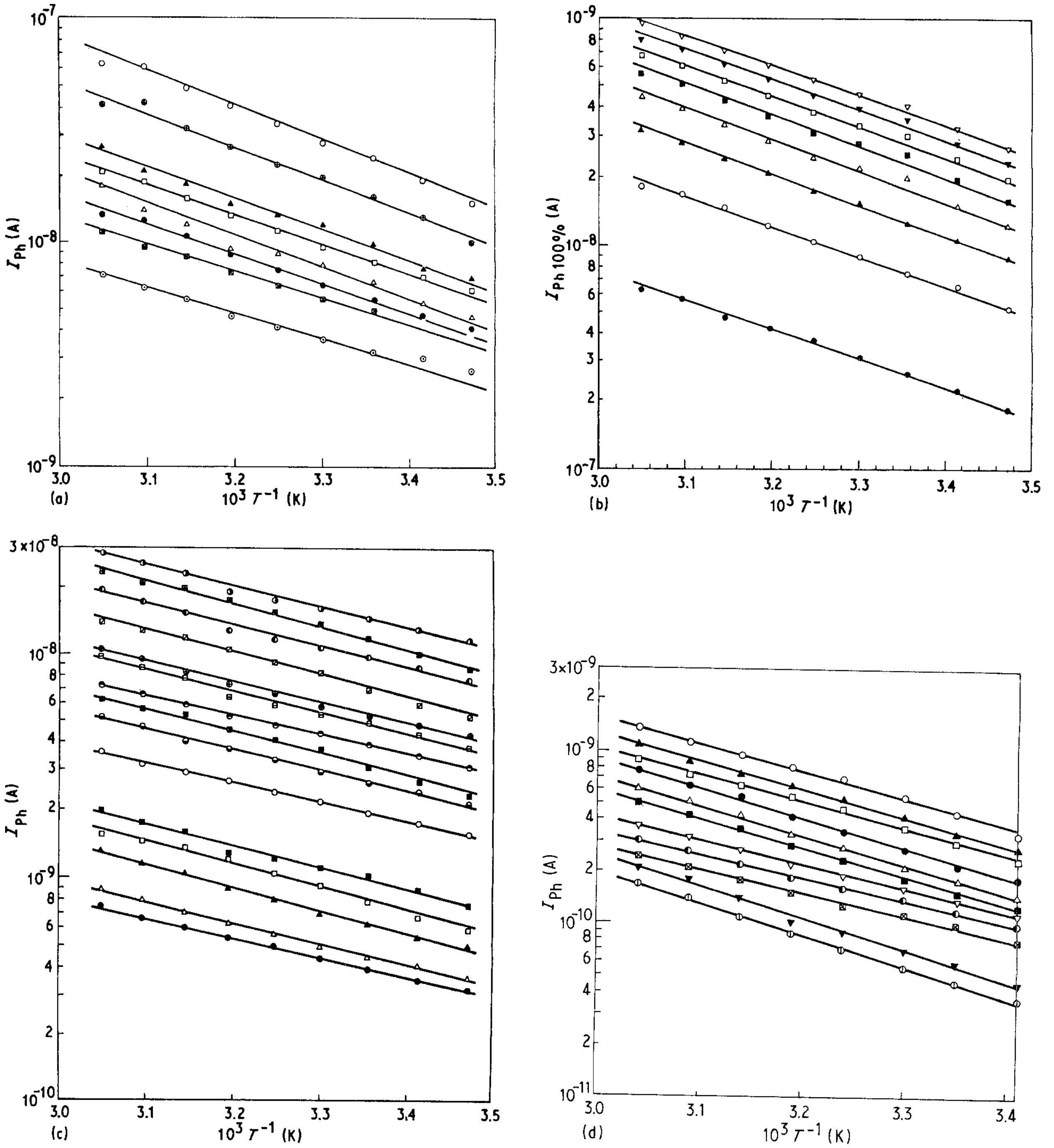

Figure 2 Plot of the logarithm of photocurrent (log(I_{Ph})) versus reciprocal of the temperature of the sample. (a) 1,4-DAAQ at different intensities of illumination: (—○—) 150 V, 100%, (—⊕—) 100 V, 100%, (—▲—) 150 V, 63%, (—□—, —●—) 100 V, 52%, (—△—) 100 V, 63%, (—⊠—, —⊙—) 100 V, 29%; (b) 1,4-DMAAQ at 100% intensity: (—●—) 10 V, (—○—) 30 V, (—▲—) 50 V, (—△—) 70 V, (—■—) 90 V, (—□—) 110 V, (—▼—) 130 V, (—▽—) 150 V; (c) 1,4-DMAAQ at 63%, 52% and 29% intensities: (—■—) 10 V, 63%, (—□—) 50 V, 63%, (—◐—) 100 V, 63%, (—◑—) 150 V, 63%, (—□—) 10 V, 52%, (—⊠—) 50 V, 52%, (—◪—) 100 V, 52%, (—⊞—) 150 V, 52%, (—△—) 10 V, 20%, (—◒—) 60 V, 29%, (—⊕—) 120 V, 29%, (—●—) 10 V, visible radiation only (472 nm max), (—○—) 50 V, visible radiation only (472 nm max), (—◓—) 100 V, visible radiation only (472 nm max), (—▲—) 10 V, UV radiation only. (d) 1,4-DHAQ at different intensities of illumination: (—○—) 150 V, 100%, (—▲—) 120 V, 100%, (—□—) 100 V, 100%, (—●—) 150 V, 63%, (—△—) 120 V, 63%, (—■—) 100 V, 63%, (—▽—) 120 V, 52%, (—◐—) 100 V, 52%, (—⊠—) 80 V, 52%, (—▼—) 100 V, 29%, (—⦶—) 80 V, 29%. I_B at 100% = 12 mW per sample.

case of 1,4-DMAAQ, the s' parameter shows two values ($s' = 0.6$–0.7 in the field region 0–2.5 kV cm^{-1} and $s' \approx 1$ in the field region 2.5–7.5 kV cm^{-1}).

The photocurrent, I_{Ph}, increases with the light intensity, I_{B}, yielding plots which follow the relation,

$$I_{\mathrm{Ph}} = bI_{\mathrm{B}}^{\gamma} \qquad (4)$$

(as shown in Fig. 2), where b is a constant and γ is the intensity parameter. For 1,4-DAAQ and 1,4-DMAAQ, there are two values of γ: one in the intensity region 29–63% illumination ($\gamma = 0.76$–1.1 for 1,4-DAAQ and 0.97–1.3 for 1,4-DMAAQ) and the other in the intensity region 63–100% ($\gamma = 1.64$–2.08 for 1,4-DAAQ and $\gamma = 1.78$–2.63 for 1,4-DMAAQ) and the value of γ being 1.3–1.5 for 1,4-DHAQ in the whole intensity region (29–100%). The γ values in the low intensity region for 1,4-DAAQ and 1,4-DMAAQ may be explained on the basis of the exciton–exciton interaction that leads to the carrier production: bimolecular recombination of the electrons and the holes is to be taken into account. It can also be explained as due to the dissociation of the triplet excitons at the impurity centres or at the electrode surface [26], or by the interaction of the triplet excitons with the trapped carriers [27], which leads to bands in the range of the triplet absorption. The bans at 534 nm and 506 nm for 1,4-DAAQ and at 632 nm and 528 nm in the case of 1,4-DMAAQ support this fact.

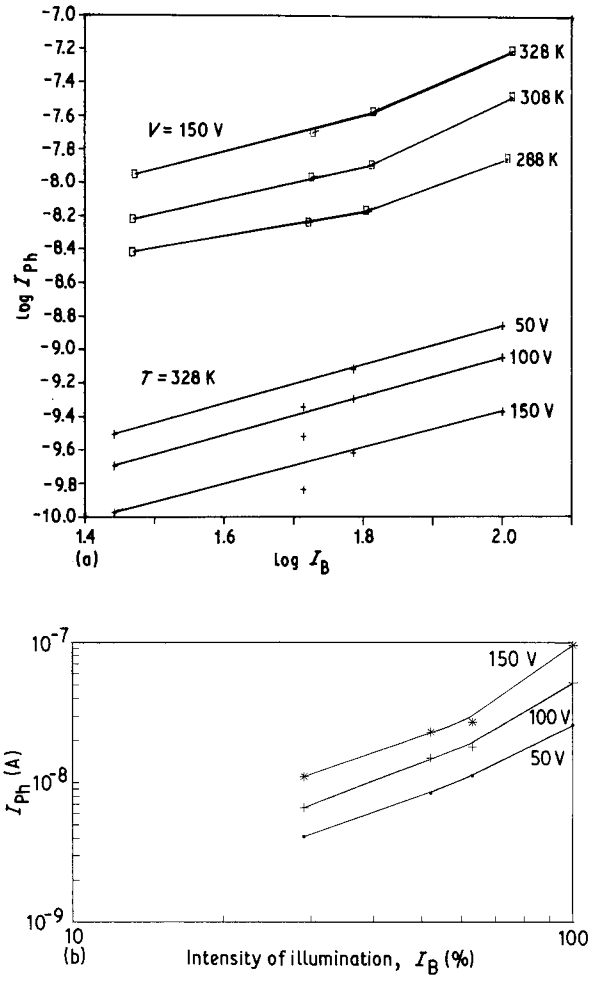

Figure 3 Logarithmic plot of intensity of illumination (log I_{B}) versus the photocurrent (log I_{Ph}) for: (a) (□) 1,4-DAAQ at an applied potential of 150 V at different sample temperatures, (+) 1,4-DHAQ at 328 K at different applied potentials and (*b*) 1,4-DMAAQ at an applied potential of 150 V at different sample temperatures. The neutral density filters made from plane quartz plates were used for varying the intensity of illumination. The intensity of light is given as a percentage (the intensity of unfiltered light being taken as 100%).

The γ values obtained at the higher intensity regions for 1,4-DAAQ and 1,4-DMAAQ and for 1,4-DHAQ over the whole intensity region can be understood in the case of negligible bimolecular recombination of carriers produced by the annihilation of the singlet excitons produced by the immediate long wavelength absorption. Along with this, the triplet excitons produced at high yields from the singlets via the intersystem crossings to the triplet state may also be important.

The participation of the defects seems not to be significant. This is supported by our recent magnetic field effect experiments in which the photocurrent increases by 2.0% in a magnetic field of about 100 mT [28].

As for the energy of activation for photoconductivity obtained from the Arrhenius relation

$$I_{\mathrm{Ph}} = A' \exp\left(-\Delta E_{\mathrm{Ph}}/kT\right) \qquad (5)$$

(where ΔE_{Ph} is the thermal activation energy of photoconduction, the values of which are given in Table I), while this could refer to either the carrier generation, the transport or both, from the low values of ΔE_{Ph} observed and the observed magnetic field effect, it may be conjectured to be due mostly to the carrier generation process. The model that seems to describe the carrier generation process may be given by diagrammatic representation as shown in Fig. 4 (p. 657 of [13]).

4. Conclusions

From the obtained results the following conclusions can be drawn:

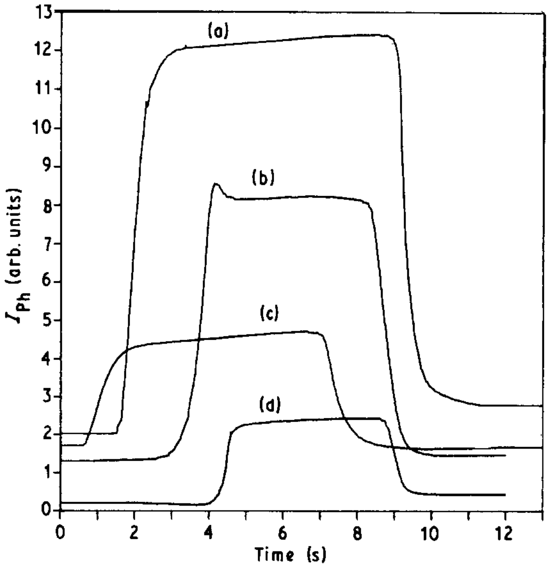

Figure 4 Rise and decay transients for compounds under discussion. The temperatures and the applied potentials at which they are recorded are given. (a) $T = 293$ K, $V = 150$ V; (b) $T = 313$ K, $V = 150$ V; (c) $T = 293$ K, $V = 25$ V; (d) $T = 313$ K, $V = 25$ V. (a), (c) 1,4-DAAQ; (b), (d) 1,4-DHAQ. Intensity of illumination is 100%.

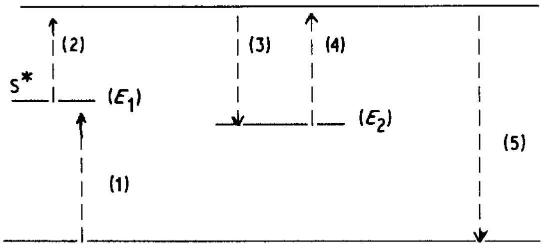

Figure 5 Energy diagram for the charge carrier generation under illumination for the dyes under discussion. Step 1 represents the excitation of the singlet states S*. Step 2 represents the dissociation of the singlet excitons at the traps. Steps 3 and 4 represent the trapping and detrapping of the charge carriers respectively. Step 5 represents the recombination of the charge carriers [28].

1. The dark current in the compounds under the present discussion are of the order of 10^{-11}–10^{-8} A.
2. The thermal activation energy of dark conduction is probably related to the depth of the traps or the impurity levels from which the charge carriers are liberated on increasing the temperature.
3. The majority of the charge carriers are electrons.
4. Due to the extrinsic nature of the charge carrier generation and the low current densities, the current–voltage characteristics are dominated by carrier recombination and not by space charge effects.
5. Evidence for the above mentioned fact has been observed from our recent magnetic field effect experiments in the mentioned compounds.

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