Photoconductivity Spectrum of Biphenyl

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Photoconductivity of biphenyl has been studied by Lyons[1] using the mercury lines at 254, 265 and 280 mμ. Kommandeur[2] and Baessler[3] have determined the photoconductivity of biphenyl in the molten state.

We have studied the bulk photoconductivity of biphenyl in a sandwich type cell, the crystal being illuminated with polarized light in the spectral region lying between 220 and 330 mμ. The light source was a Xenon lamp (OSRAM XBO 900); the light was monochromatized by a Hilger & Watts grating monochromator and polarized by a glan-air polarizing prism. Single crystals have been used, whose thickness ranged from 100 to 140 μ. They were obtained by sublimation of the substance wich had been previously purified by means of chromatography and zone refining (20 passes). Measurements have been carried out in d.c., and solutions either of KCl, or HCl, or KOH 0,1 M were used as transparent electrode; the second electrode was "aquadag". The maximum sensitivity of our measurements was 10^{-14} A.

Figure 1 a shows the absorption spectra of single crystals of biphenyl with respect to the two crystallographic directions *a* and *b*[4]. Figures 1 b, 1 c, 1 d show the photoconductivity spectra of biphenyl, which were obtained by illumination of the positive electrode; the photocurrent was normalized to equal light quanta of incident light.

Data relative to one crystal are given in Table I; these data are not exactly reproducible for all the crystals; however the qualitative trend is always the same.

The lowest photocurrent values were obtained when the positive electrode used was the alkaline solution.

The photocurrent is directly proportional to the light intensity for different wavelengths corresponding to a maxi-

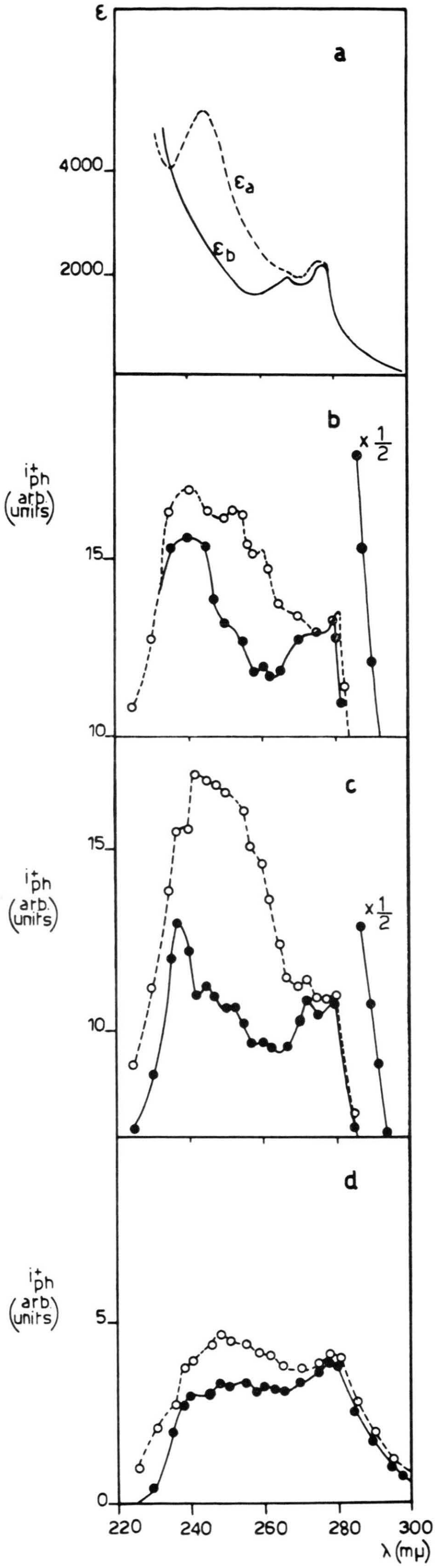

Fig. 1. a) Absorption spectrum of single crystals[4]. b) Photoconductivity spectrum; the positive electrode (HCl 0.1 M) is illuminated. c) Photoconductivity spectrum; the positive electrode (KCl 0.1 M) is illuminated. d) Photoconductivity spectrum; the positive electrode (KOH 0.1 M) is illuminated. The dotted curves refer to light polarized // *a*-axis of the crystal; the full drawn curves refer to light polarized // *b*-axis of the crystal.

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Electrode solution	λ (mμ)	Photons / sec. cm^2	i^+ (A/cm^2) $//a$-ax	i^+ (A/cm^2) $//b$-ax	i^- (A/cm^2) $//a$-ax	i^- (A/cm^2) $//b$-ax
HCl 0.1 M	250	7.3×10^{11}	1.2×10^{-10}	9.2×10^{-11}	$< 10^{-13}$	$< 10^{-13}$
	308	2.1×10^{13}	6.4×10^{-11}	6.4×10^{-11}	7.0×10^{-11}	7.0×10^{-11}
KCl 0.1 M	250	7.3×10^{11}	1.2×10^{-10}	7.3×10^{-11}	$< 10^{-13}$	$< 10^{-13}$
	308	2.1×10^{13}	4.8×10^{-11}	4.8×10^{-11}	7.0×10^{-11}	7.0×10^{-11}
KOH 0.1 M	250	7.3×10^{11}	3.8×10^{-11}	2.9×10^{-11}	$< 10^{-13}$	$< 10^{-13}$
	308	2.1×10^{13}	4.8×10^{-11}	4.8×10^{-11}	7.0×10^{-11}	7.0×10^{-11}

Table 1. Photocurrent values obtained in a crystal whose thickness is of 140 μ; the applied voltage is 100 V; the surface area of the illuminated electrode is equal to 3.14×10^{-2} cm^2.

mum and a minimum in the absorption. This holds for the range of the used intensities (1×10^{11} hν/cm^2 sec to $2{,}2 \times 10^{13}$ hν/cm^2 sec). The photocurrent i^+ is not linearly dependent on the applied voltage; i^+ tends to saturate with voltage for fieldstrength exceeding 2.10^4 V/cm at wavelengths lying between 260 and 300 mμ.

Figures 1a, 1b, 1c, and 1d show that the shape of the photoconductivity spectrum closely resembles that of the absorption spectrum. The figures show that i^+ and the peak-to-valley ratios are highly dependent on the electrode used. This is in agreement with the assumption made for anthracene[5], i.e. i^+ being injected by the electrodes. It may be assumed that also for biphenyl, the mechanism for charge production involves the migration of neutral excitions to the surfaces, their annihilation at the surface and the injection of a positive charge into the crystal[6,7].

A consequence of the above mentioned mechanism[8] is that the plot of the inverse photocurrent vs. the inverse absorption coefficient gives a straight line, when the photocurrent is near to saturation; this is what we have found in our particular case (Fig. 2). From the slope of the lines in Fig. 2 the excitions diffusion length is calculated to be about 5600 Å with alkaline electrode and about 4300 Å with acidic electrode.

The photoconductivity spectrum that we have obtained by illumination of the negative electrode shows only one maximum (Fig. 3) at 308 mμ, which corresponds to a region of low absorption by the crystal. We think that the energetic conditions available do not allow to inject electrons into the crystal. The peak at 308 mμ might be attributed to the release of space charges in the region near the electrode opposite to that one which is illuminated, which is in accordance with Kommandeur and Schneider[9]. This assumption appears to be confirmed by the fact that the peak intensity decreases when the thickness of the crystal increases.

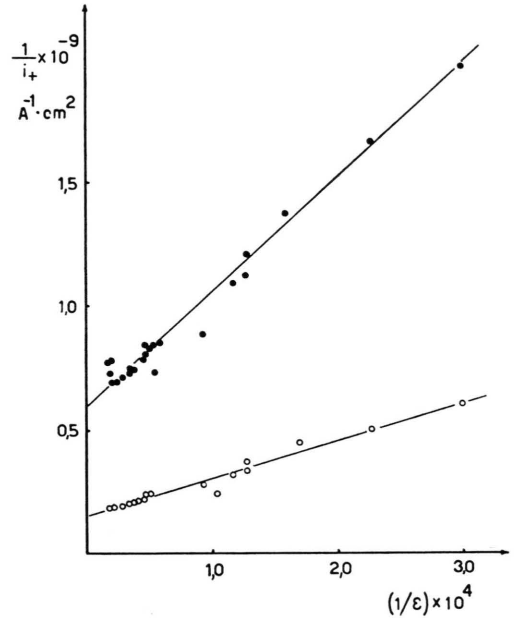

Fig. 2. Plot of the inverse photocurrent vs. $1/\varepsilon$ for acidic (empty circles) and alkaline (full circles) electrodes.

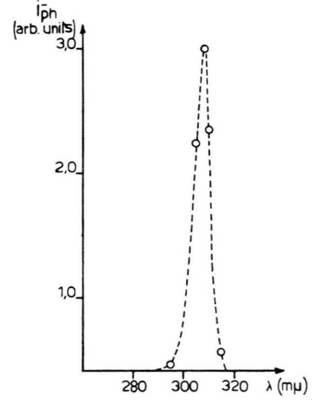

Fig. 3. Photoconductivity spectrum; the negative electrode is illuminated. The arb. units are the same as in Fig. 1.

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