Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

Gabriele Giro, Pier Giulio Di Marco

Electrical conductivity of biological and organic compounds. Part. V. Photoconductivity spectra of some heterocyclic compounds

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **51** (1971), n.5, p. 371–376.

Accademia Nazionale dei Lincei

<http://www.bdim.eu/item?id=RLINA_1971_8_51_5_371_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1971.

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Electrical conductivity of biological and organic compounds*. Part. V. *Photoconductivity spectra of some heterocyclic compounds* (*). Nota di GABRIELE GIRO (**) e PIER GIULIO DI MARCO (**), presentata (***) dal Socio G. SEMERANO.

RIASSUNTO. — In questa Nota vengono riportati gli spettri di fotoconducibilità del dibenzotiofene(I), dibenzofurano(II), carbazolo(III) e fluorene(IV) nella regione compresa fra 250–350 mμ. Tutte le misure sono state eseguite adoperando celle del tipo a superficie. Gli spettri di fotoconducibilità di (I), (II), (III) e (IV) riproducono abbastanza fedelmente gli spettri di assorbimento ottico.

INTRODUCTION

The relationship between photoconductive properties of organic materials and fluorescence are not yet known; however, it is well known that many good photoconductors have a good fluorescence quantum yield and fluorescence quenchers are also photoconductivity quenchers. In order to find a quantitative relationship between these properties, a study on the heterocyclic compounds dibenzothiophene, dibenzofuran, carbazole and fluorene has been initiated. Such substances differ in the type of heteroatom and thus are suitable for comparative measurements. The fluorescent properties of these compounds are known [1, 2], but the photoconductive properties have not yet been determined.

In contrast with the results obtained by Mukherjee [3], it was possible to obtain photoconductive effects and to determine photoconductivity spectra. In obtaining these results surface cells similar to those employed by other Authors were used after certain modifications.

EXPERIMENTAL SECTION

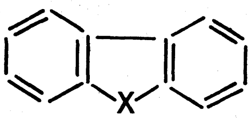
The substances (I), (II), (III) and (IV) were first purified by chromatography, sublimation [4, 5] and then zone refined (80 passes). A purity test was done after each step of the purification procedure. The electrical measurements were made by using surface cells, consisting of a quartz plate, onto which two aluminium electrodes had been evaporated, 1 mm apart.

(*) Work carried out with the financial help of C.N.R.

(**) Laboratorio di Fotochimica e Radiazioni d'Alta Energia – Bologna.

(***) Nella seduta del 13 novembre 1971.

The electrodes used were: *a*) opaque to the incident light; *b*) semitransparent. For the cells with semitransparent electrodes, optical absorption measurements were done to obtain comparable results.



	-X-	compound
(I)	-S-	dibenzothiophene
(II)	-O-	dibenzofuran
(III)	-NH-	carbazole
(IV)	$-CH_2-$	fluorene

The substances were evaporated on the cells.

The photocurrents were measured in the region between 250–350 mμ under vacuum (10^{-3} Torr). For details of measurement apparatus, see previous works [6, 7].

EXPERIMENTAL RESULTS AND DISCUSSION

Measurements of steady state photocurrents were carried out in the following way:

a) Opaque electrodes (fig. 1 A): The photoconductive effect on (I), (II), (III) and (IV) is negligible and therefore it was not possible to obtain different photoconductivity values, when the wavelength was changed.

b) Semitransparent electrodes (fig. 1 B): Substances (I), (II), (III) and (IV) all show photoconductive properties such that a complete spectrum of photoconductivity can be obtained.

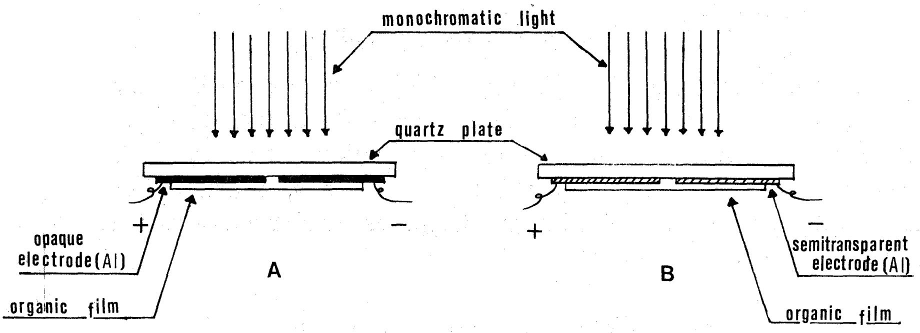


Fig. 1. – Two version of test cells. A: surface cell with opaque electrodes; B: surface cell with semitransparent electrodes.

Under the prevailing operating conditions, using semitransparent electrodes results in a greater illuminated surface and a larger contact area with the substance than in the case of opaque electrodes, and consequently even if the recombination rate is high, a number of charges sufficient to produce photocurrent is obtained.

The results presented in *a*) and *b*) can both be explained on the basis of two different charge generation mechanisms, i.e.:

i) Exciton-surface mechanism;
ii) Direct generation mechanism.

As far as the first mechanism is concerned, its validity seems to emerge from the analogy between photoconductivity spectrum and electronic absorption spectrum [8]. The second one may be considered only if one assumes a very high recombination rate. In fact, if this is the case, the mean free path of the charges is very low and, therefore, only the charges whose distance from the electrodes is lower or at most equal to the mean free path, can give rise to photoconductivity. As a result, with opaque electrodes the charges generated in the proximity of the electrodes at a distance less than the mean free path are less than those generated in the case of semitransparent electrodes.

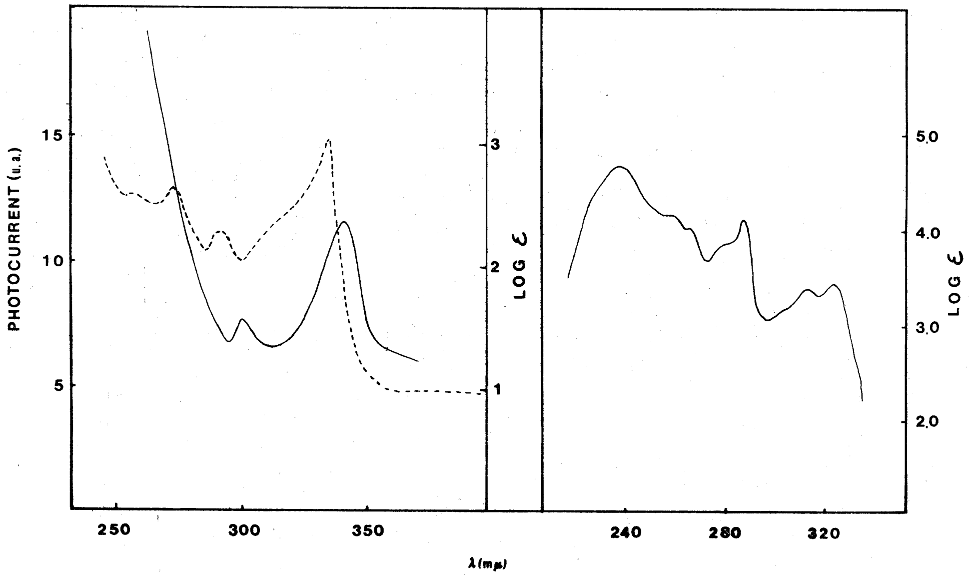


Fig. 2. – Left: solid curve, photoconductivity spectrum of substance (I); dashed curve, optical absorption spectrum of (I) in solid [3]. Right: optical absorption spectrum of (I) in solution [10].

In figs. 2, 3, 4 and 5, the dependence of photocurrents on wavelength is reported for dibenzothiophene, dibenzofuran, carbazole and fluorene.

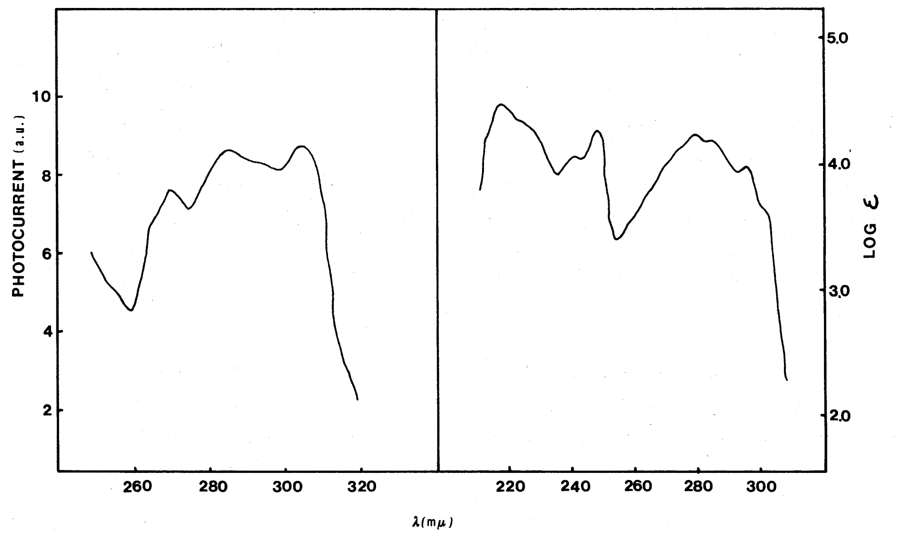


Fig. 3. – Left: photoconductivity spectrum of substance (II). Right: absorption electronic spectrum in solution of (II) [10].

In all experiments an electric field of 5000 V/cm was used. The photoconductivity values, of the same substances measured at the same conditions of light intensity and voltage, are reported in Table I.

TABLE I.

Surface photocurrent data for some heterocyclic compounds [a,b].

COMPOUND	Photocurrent (A)	Excitation wavelength (mμ)
Dibenzothiophene	0.125×10^{-11}	340
Dibenzofuran	0.650×10^{-12}	305
Carbazole	0.150×10^{-12}	335
Fluorene	0.200×10^{-13}	300

(*a*) Field applied: 5000 V/cm.
(*b*) The light intensity was kept constant by varying the output slit of monochromator.

The photoconductivity spectrum of dibenzothiophene presents two maxima (340 and 300 mμ) that closely follow the optical absorption spectrum in solid [3]. This result is in good agreement with data obtained by other workers [3]. Compared to the optical absorption spectrum in solution the spectrum in solid shows that the bands in the 250–350 mμ region are shifted towards the red (fig. 2).

Dibenzofuran, carbazole and fluorene photoconductivity spectra are shown in figs. 3, 4 and 5 respectively and optical absorption spectra in solution have the same behaviour. We consider it desirable to compare the photoconductivity

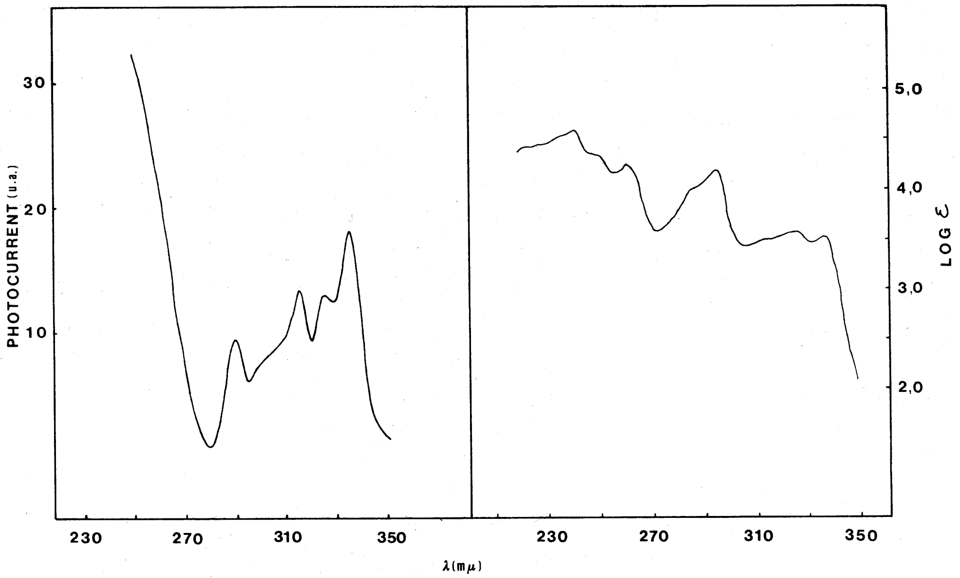


Fig. 4. – Left: photoconductivity spectrum of substance (III). Right: absorption electronic spectrum of (III) in solution [9, 10].

spectra with optical absorption spectra in the solid for all the compounds of the series investigated and this will be the subject of a future work.

By a comparison of the photocurrent values shown by (I), (II), (III) and (IV) it can be seen that dibenzothiophene, dibenzofuran and carbazole exhibit some orders of magnitude photoconductivity response larger than fluorene. If we consider, the structures of (I), (II) or (III) and compare with

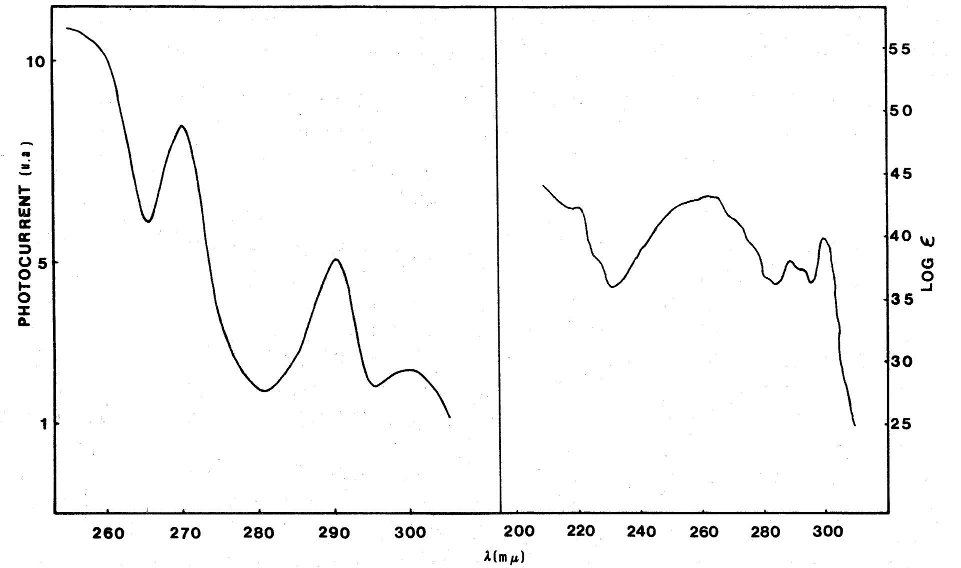


Fig. 5. – Left: photoconductivity spectrum of substance (IV). Right: absorption electronic spectrum of (IV) in solution [9].

that of (IV), we see that in fluorene the methylene carbon uses sp^3 orbitals and the $C = H_2$ electrons on this tetrahedral carbon atom are not delocalized. On the other hand, in the dibenzothiophene, carbazole and dibenzofuran, the lone-pair electrons on the heteroatom are largely "*p*" in character and hence coalesce with the cloud on the adjacent benzenoid rings. The character of lone pair electrons of the heteroatom in (I), (II) and (III) characterizes these substances as "Aromatics" and this aromatic behaviour should explain the larger photoconductivity of (I), (II), (III) in comparison with (IV).

It is interesting also to note that there is a reverse relationship between the fluorescence quantum yield [1] of (I), (II), (III) and (IV) and their photocurrent values. In fact the fluorescence quantum yield decreases from fluorene, carbazole, dibenzofuran and dibenzothiophene, instead there is evidence for a photocurrent increase from fluorene to dibenzothiophene. See Table II.

TABLE II.

Photocurrent data comparison with fluorescent quantum yield for some heterocyclic compounds.

COMPOUND	Fluorescence quantum yield	Photoconductivity values (A)
Dibenzothiophene	0.03	0.125×10^{-11}
Dibenzofuran	0.29	0.650×10^{-12}
Carbazole	0.35	0.150×10^{-12}
Fluorene	0.50	0.200×10^{-13}

Further experiments on these substances are in progress. The purpose is to study the nature of charge generation, recombination, photoconductivity quantum yields, lifetimes and drift mobilities of charge carriers.

The Authors are indebted to Prof. G. Semerano for his encouragement and useful discussions throughout the present work.

REFERENCES

[1] D. W. ELLIS and B. S. SOLOMON, « J. Phys. Chem. », *46*, 3497 (1967).

[2] S. P. MC. GLYNN, T. AZUMI and M. KINOSHITA, *Molecular spectroscopy of the triplet state*, Prentice-Hall, Inc., Englewood Cliffs, N.J. (1969).

[3] T. K. MUKHERJEE, « J. Phys. Chem. », *74*, 3006 (1970).

[4] A. BREE and R. ZWARICH, « Spectrochimica Acta », *25A*, 713 (1969).

[5] R. C. SANGSTER and J. W. IRVIN JR., « J. Chem. Phys. », *24*, 670 (1956).

[6] G. GIRO, P. G. DI MARCO, F. BOLLETTA and S. DELLONTE, « Chimica e Industria », *53*, 342 (1971).

[7] P. G. DI MARCO, F. BOLLETTA, S. EMMI and G. GIRO, « Chimica e Industria », *53*, 571 (1971).

[8] O. H. LE BLANC JR., *Physics and Chemistry of Organic Solid State*, D. R. Fox and M. M. Labes, A. Weissberger Eds. Vol. 3°, Interscience, N.Y. (1965).

[9] R. A. FRIEDEL and M. ORCHIN, *Ultraviolet spectra of aromatic compounds*, John Wiley and Sons, N.Y. 1951.

[10] G. M. BADGER and B. J. CHRISTIE, « J. Chem. Soc. », 3438, (1956).