Electrical Conductivity of *o*-, *m*-, and *p*-Terphenyls

P. Costa BIZZARRI and C. DELLA CASA

Istituto di Chimica degli Intermedi, Facoltà di Chimica Industriale,
Università di Bologna, Italy

and

S. PIETRA

Istituto Chimico, Facoltà di Ingegneria, Università di Bologna, Italy

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Many investigations have been carried out on the electrical properties of *p*-terphenyl¹⁻⁹, and, as far as we know, only one on *m*-terphenyl¹⁰. In the present work, the d. c. electrical conductivities of the three isomeric terphenyls are compared to establish the influence of the molecular structure on the electrical properties and to explain the mechanism of the energy transport in organic molecules.

Experimental

Monocrystals of the samples were obtained from solutions after purification by recrystallization, chromatography¹¹, and zone melting. Careful analyses on irradiated samples of *o*-terphenyl rule out the presence of triphenylene. Samples of *m*-terphenyl free from *p*-isomer were supplied by RISALITI¹².

The d. c. measurements were carried out by a volt-ampereometric method in an atmosphere of flowing anhydrous nitrogen. The electric field in the case of *m*-terphenyl was applied in the {201} plane for the surface current and perpendicular to this plane for the bulk current. For *p*-terphenyl, the electric field was in the {001} plane for the surface current and perpendicular to this plane for the bulk current. The electrodes consisted of Ag paste. In photoconductivity measurements the transparent electrode (positive) was formed by 1 N HCl. For the irradiation of the crystals, the light from a 900 W xenon lamp was monochromatized with a Bausch & Lomb grating. Light flux falling on the sample: ≈ 0.5 mW/cm². The light current was measured at the wavelengths of the UV absorption maxima¹³. Dielectric constants (1 kHz, room temperature): *o*-Terphenyl, $\epsilon = 2.2$; *m*-terphenyl, $\epsilon = 2.4$; *p*-terphenyl, $\epsilon = 2.1$.

Results and Discussion

A SCHOTTKY effect may be responsible for the

charge injection into *o*-terphenyl crystals; the linearity of the relationship between the surface current density and the square root of the applied field (Fig. 1) confirm our opinion. The surface photo-

Fig. 1. Plot of the surface dark current density against the square root of the applied field for *o*-terphenyl.

conductivity at $\lambda < 250$ m μ can be explained as a contribution of the light energy to the lowering of the SCHOTTKY barrier between the crystal and the electrode (Ag paste).

The plot of the bulk current density against the applied field is very different when 1 N HCl electrode is used instead of Ag electrode (Fig. 2); this points

Requests for reprints should be sent to Dr. S. PIETRA, Istituto Chimico, Facoltà di Ingegneria della Università di Bologna, Viale Risorgimento, 2, I-40136 Bologna, Italy.

Fig. 2. Plot of the bulk dark current density against the applied field for *o*-terphenyl. (○) Ag electrode; (□) 1 N HCl electrode.

to a different charge injection mechanism. Both currents are SCL. To calculate the mobility we can apply the formula given by BOON¹⁴ for an *hopping* transport of the charge carriers:

$$J = \frac{9}{16} \epsilon \epsilon_0 \mu \frac{E^2}{d} \quad (1)$$

where ϵ_0 is the dielectric constant of free space, μ the mobility, E the applied field, and d the electrodes distance. We obtain: $\mu \geq 2 \cdot 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

In the case of *m*-terphenyl, a definite photoconductivity is found for the surface and bulk currents. Its maxima correspond to the UV absorption maxima. The dark currents are SCL, and application of (1) gives a surface mobility $\mu_s \geq 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($E = 2100 \text{ V cm}^{-1}$), and a bulk mobility $\mu_b \geq$

$5 \cdot 10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ($E = 30,000 \text{ V cm}^{-1}$). In comparison with the data found by RAMAN and MCGLYNN¹⁰, it should be remembered that there is a difference of one order of magnitude between the values of μ found from the SCLC curves and those obtained by the transient current method¹⁵. Calculation of the apparent activation energy gives a value $E_{a1} \approx 0.5 \text{ eV}$ for the range $20\text{--}45^\circ\text{C}$ and $E_{a2} = 1.6 \text{ eV}$ for the range $45\text{--}85^\circ\text{C}$.

In the case of *p*-terphenyl, our measurements are in substantial accord with those of other authors. A trap concentration of $N_T = 8 \cdot 10^{14} \text{ cm}^{-3}$ is calculated from the SCLC. Measurements carried out in the temperature range $20\text{--}85^\circ\text{C}$ give an apparent activation energy $E_a = 0.48 \text{ eV}$, that is an impurity level⁹.

In some samples of *p*-terphenyl with irregular crystal structures, we have found that the current changes rapidly from 10^{-10} A to 10^{-6} A at electric fields of about $4 \cdot 10^4 \text{ V cm}^{-1}$. This effect is reproducible, and is influenced by the temperature (the transition voltage decreases with rising temperature). The dependence of the bulk current density on the applied field is ohmic in the region of low resistivity, and the interruption of the voltage for some time (1 or 2 hours) leads back to the region of high resistivity. We may attribute this phenomenon either to the FRENKEL-POOLE effect or to emptying of the traps¹⁶.

From the experimental results in Tables I and II, it can be seen that the dark conductivities J increase in the order *para* < *meta* < *ortho*, and the photoconductivities J_{ph} follow the order *ortho* < *meta* < *para*. The latter increase is parallel to the

Table I. Surface measurements.

	E [V cm ⁻¹]	$J \cdot 10^{13}$ [A cm ⁻²]	J_{ph}/J	E [V cm ⁻¹]	$J \cdot 10^{12}$ [A cm ⁻²]	J_{ph}/J
<i>o</i> -terphenyl	500	230	0.13	2000	700	0.11
<i>m</i> -terphenyl	500	21	0.86	2000	15	0.33
<i>p</i> -terphenyl	500	1.4	1.21	2000	1	0.90

Table II. Bulk measurements with 1 N HCl electrode.

	E [V cm ⁻¹]	$J \cdot 10^{10}$ [A cm ⁻²]	J_{ph}/J	E [V cm ⁻¹]	$J \cdot 10^{10}$ [A cm ⁻²]	J_{ph}/J
<i>o</i> -terphenyl	10 000	25	—	—	—	—
<i>m</i> -terphenyl	10 000	4.3	0.01	40 000	40	0.05
<i>p</i> -terphenyl	10 000	2	0.15	40 000	2.2	3.9

extension of the conjugation between the aromatic rings¹³. The different order of increasing of the dark conductivities may be attributed to the different crystal directions of the measured currents.

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