Electronic Properties of Quaterrylene, $C_{40}H_{20}$

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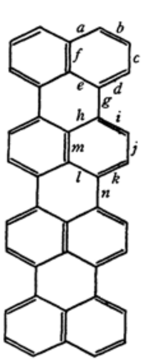
Experimental studies of the electrical and optical behaviour of organic semiconductors have been carrried out for a number of materials.[1] In the polycyclic aromatic hydrocarbon series quaterrylene, $C_{40}H_{20}$ (Fig. 1), with eleven benzene rings, is one of the largest molecules ever studied as an organic semiconductor.



Average lengths

$a=1.392\pm0.009$ Å
$b=1.374\pm0.007$
$c=1.425\pm0.004$
$d=1.405\pm0.008$
$e=1.396\pm0.012$
$f=1.432\pm0.015$
$g=1.526\pm0.007$
$h=1.405\pm0.015$
$i=1.366\pm0.012$
$j=1.425\pm0.018$
$k=1.379\pm0.008$
$l=1.408\pm0.005$
$m=1.430\pm0.009$
$n=1.529\pm0.006$

Fig. 1. Quaterrylene ($C_{40}H_{20}$).

Quaterrylene was synthesized by Clar et al.[2] and also by Zinke and his coworkers.[3] Though there is some confusion between them it generally seems to be true that it is synthesized by a condensation of perylene. The crude material applied in the work was provided by Rütgerswerke-Aktiengeselschaft A. G., Germany, and was regarded as "Clar's quaterrylene" on the basis of its optical absorption spectra.

The crystal and molecular structure of quaterrylene (Clar's quaterrylene) was studied by Shrivastava and Speakman[4] in connection with X-ray analysis. They found that quaterrylene is isotypic with perylene; it crystallizes in the monoclinic system with $a=11.25$ Å, $b=10.66$ Å, $c=19.31$ Å, $\beta=100.6°$ and with four molecules per unit cell, while the space group is $P2_1/a$. The molecule lies with its greatest length almost exactly perpendicular to the ab plane. The bond lengths are shown in Fig. 1; the mean length of the peri-bonds connecting the naphthalenic residues is assessed at 1.53 ± 0.01 Å.

An aromatic compound with a larger molecular size would have a higher electrical conductivity. Therefore, it is expected that reliable results concerning semiconductive behaviour would be found when this hydrocarbon is applied for the observations of Shrivastava and Speakman. In this article, we are presenting a more quantitative figure of organic semiconductors obtained through a study of the electronic properties of quaterrylene.

Further, the simple molecular orbital calculation for this molecule will in due course enable the present authors to explain its spectroscopical data.

Experimental Procedures

Purifications.—The microcrystals of quaterrylene were dark green, but its thin films were violet. The hydrocarbon was extraordinarily stable, as it could be heated to about 500°C without decomposition and without melting. Since they were virtually insoluble in all solvents at room temperature, ordinary methods for the purification of organic compounds, for recrystallization and for chromatography could not be applied. Therefore, sublimation was the most useful technique for purification and also for making single crystals in this case.

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[1] H. Inokuchi and H. Akamatu, "Solid State Physics," Vol. 12, Academic Press, New York (1961), p. 93.

[2] E. Clar, W. Kelly and R. M. Laird, *Mh. Chem.*, **87**, 391 (1956).

[3] A. Zinke, H. Nussmuller and R. Ott, ibid., **86**, 853 (1955); A. Zinke, E. Zeschko and R. Ott, ibid., **91**, 445 (1960).

[4] H. N. Shrivastava and J. C. Speakman, *Proc. Roy. Soc.*, **257**, 477 (1960).

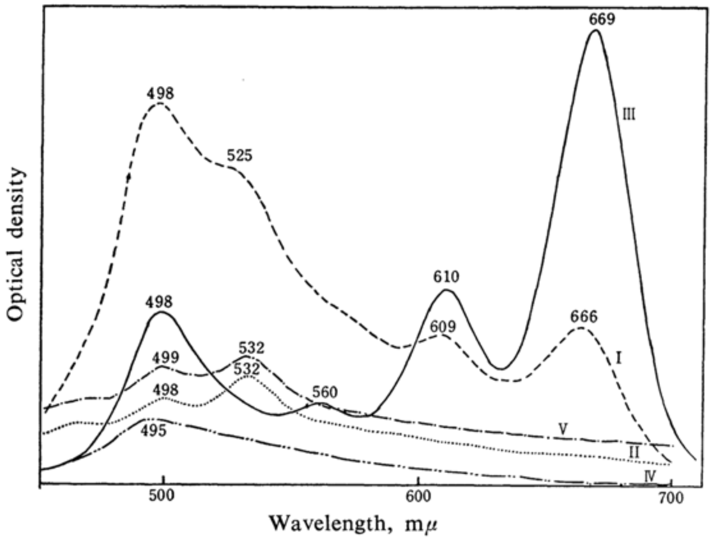


Fig. 2. The optical absorption spectra in the course of purification.

Impurities included in the matrix were soluble in trichlorbenzene. Therefore, the filtration technique was also employed for purification. Before filtration, the hydrocarbon was sublimed three times in vacuum of 10^{-5} mmHg at about 450°C. The compound was also dark green-coloured microcrystals. A suspension of quaterrylene in trichlorobenzene possessed no absorption peaks in a visible region because of its insolubility at room temperature. It was rather soluble in that solvent at about 100°C; the solution was blue at that temperature. The absorption spectrum for this step is shown as curve I in Fig. 2. When the hot solution was cooled, its colour changed to a light reddish violet from blue and dark green powders were precipitated. This spectrum is shown as II in Fig. 2. The powders which were filtered off from the solution were suspended again in cold trichlorobenzene. No absorption peaks could be found in the spectrum at room temperature, but at about 100°C several peaks appeared on the spectral response curve. The spectrum is shown as III in the figure.

A remarkable difference between curves I and III is the disappearance of the peak of 525 mμ in the latter spectrum. When the solution was cooled, only the peak of 495 mμ survived (curve IV). On the other hand, the filtered solution possessed 499 mμ and 532 mμ absorption peaks (curve V), and no considerable change in spectra was obtained by means of heating and cooling.

In order to examine the solvent effect on the absorption spectra, α-methylnaphthalene was employed in place of trichlorobenzene. This spectrum is illustrated as curve VI, which corresponds to curve I. Since no noticeable difference could be found between them, it can be concluded that the solvent effect is to be neglected.

When III and V are compared, it seems that the 530 mμ peak originates in impurities which are soluble in cold trichlorobenzene. On the basis of these results, the typical absorption spectrum of quaterrylene is possibly curve III: this agrees with the finding of Clar.[2]

The absorption spectrum of the evaporated thin film is shown in Fig. 3, along with that of the solution.

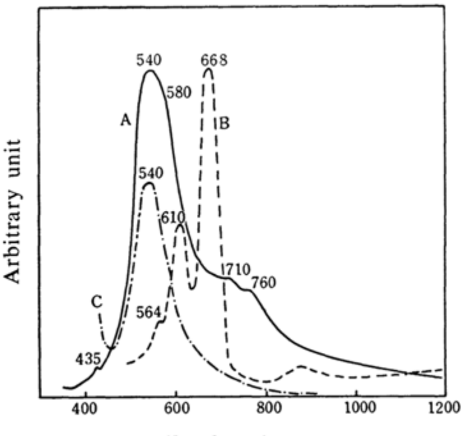


Fig. 3. The optical absorption spectra of thin film (A) and of solution (B) of quaterrylene. Curve C shows the spectral response of photo-emf.

In ordinary aromatic hydrocarbons, the positions of their absorption peaks for the solid state only shift to the long wave length side compared with those for the solution state. For quaterrylene, however, this was not the case, and, further, no correspondence between their absorption peaks and the intensity ratios of both their spectra was found.

Preparation of Single Crystals.—Because of the insolubility of quaterrylene for any solvent, it was difficult to obtain a single crystal sufficient in size to measure the resistivity by deposition from a

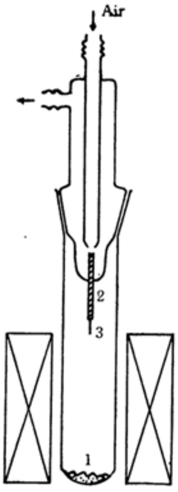
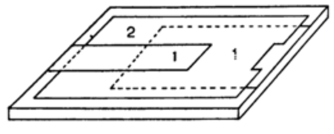


Fig. 4. The sublimation vessel used to make single crystals.

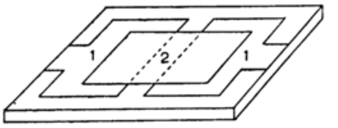
solution or by cooling the molten material. Thereby, a slow sublimation of quaterrylene in a vacuum vessel, as is shown in Fig. 4, was applied to make a single crystal. The bottom (1) of a glass tube which had been evacuated to a pressure of 10^{-5} mmHg was heated by a surrounding electric furnace. Before starting the sublimation, a tiny needle-like single crystal (3) to be used as a nucleus was stuck on the top of the tungsten rod (2), which is cooled with circulated air. Upon being heated at 350°C for a long period, the single crystal grew to a fairly large one, 0.2 mm. × 0.2 mm. × 5.0 mm. The direction of the long axis of the crystal was b.

Preparation of Conductivity Cells.—The cells of the thin film of quaterrylene were prepared by the method of vacuum evaporation. When the evaporation speed was controlled to be slow, the prepared films were lustrously violet and very stable. They seemed to be better-oriented films than those of other aromatics. Thin aluminium or silver films which had also been evaporated in vacuo were employed for the electrodes of cells, as is shown in Fig. 5.

The powdered specimens compressed in an insulating cylinder were also applied measured for resistivity.



(1) Sandwich-type



(2) Surface-type

Fig. 5. The electrode arrangement of cells. Electrodes (1) and quaterrylene (2).

Preparation of the Single Crystals for a Polarized Light Absorption.—In the course of the vacuum evaporation of quaterrylene, when a substrate, a glass plate, was heated to the proper temperature from the back by an electrical heater, fairly large single crystals grew on the film. In fact, the evaporation had to proceed very slowly in this case; it took several hours to accomplish it under a pressure of 10^{-5} mmHg.

For that duration, the substrate was kept at about 250°C, and the evaporation gun, at about 450°C. Following this method, one or two flat single crystals $50\,\mu \times 100\,\mu \times 100\,\text{Å}$ (thickness) could be found on the film under a polarization microscope, and, as they showed oblique extinction, the crystal faces were possibly ac plane. It is expected that the polarized light absorption spectra of these crystals will probably show dichroism and "Davydov Splitting."

Experimental Results

The measurements of the electrical resistivity were made with a Cary vibrating-reed electrometer, model 31, for four types of specimens; compressed powders, single crystals, sandwich-type films, and surface-type films. For the last two types of cells, the photoconductivity measurements were also made using a Hitachi photo-electric spectrometer, model EPU-2, or a projector lamp as the light sources. Their dark resistivities are listed in Table I.

TABLE I. THE ELECTRICAL RESISTIVITY, ρ_{15} OF QUATERRYLENE $\rho=\rho_0 \exp(\Delta\varepsilon/2\boldsymbol{kT})$

Type of specimen	ρ_{15}, Ωcm.	$\Delta\varepsilon$, eV.
Powder	10^{10}	0.6
Single crystal	10^{6}	—
Sandwich-type	10^{13}	0.6
Surface-type	10^{5}	0.6

From the results of the two types of film cells, a substantial anisotropy of the resistivity was found by a factor of $10^7 \sim 10^8$; 10^5 Ωcm. for the surface-type cell and 10^{13} Ωcm. for the sandwich-type cell.[5] The $\Delta\varepsilon$ values listed in the same table were calculated from the temperature dependence of the resistivity in the range of 15∼150°C in air.

Quaterrylene was very stable against an applied electric field; the hydrocarbon could be subjected to a very high voltage, $10^6 \sim 10^7$ V./cm. The relation between the dark current and their applied potential is given in Fig. 6.

In the sandwich-type cell, a photovoltage appeared when it was illuminated by a visible light. As the photoelectromotive force (abbreviated as photo-emf.) originates in the

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[5] H. Inokuchi, H. Kuroda and H. Akamatu, This Bulletin, 34, 749 (1961).

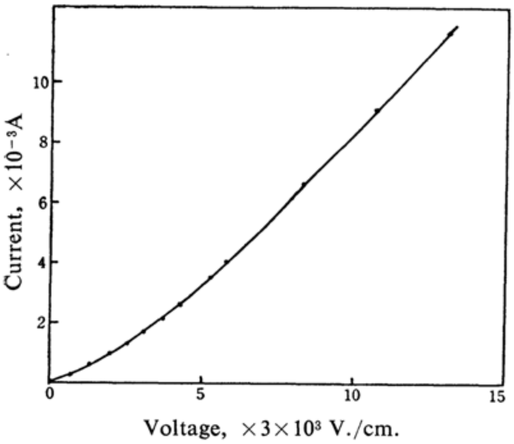

Fig. 6. The dark current versus the applied potential for the sandwich-type cell.

contact layer between the metal and the aromatics, the surface conditions of both are essential to this effect. Therefore, during the preparation of the cell and also during the measurement of the voltage, it must be kept in vacuo.* The apparatus which is convenient for such treatments is in preparation; therefore, the following data concerning photo-emf. are tentative.

In the present experiment the photovoltaic cell was made of a quaterrylene thin film sandwiched between two aluminium films on a glass plate. However, it was exposed to air for only a few minutes needed to place it in the other vessel for measurement. The photovoltage attained the maximum value of 135∼270 mV. when the light intensity was 40 μW/cm^2. The cells were sensitive to a very weak light;* the dependence on the light intensity is shown in Fig. 7. The spectral response of photo-emf. is in Fig. 3 compared with the optical absorption spectrum for the film.

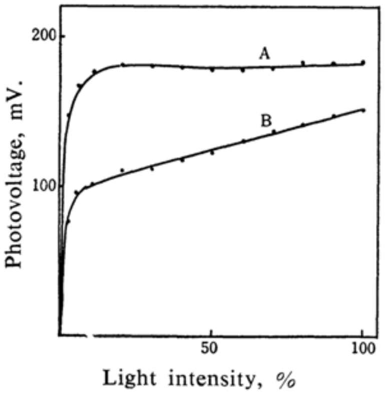

Fig. 7. The photovoltage versus the light intensity. Curve (A) is illuminated from the front of the cell and (B), from the back.

Photoconductivity measurements were also made for the surface-type and the sandwich-type cells; the former was less sensitive than the latter. The rectifying effect of the photoconduction was scarcely recognized; therefore, it could not be determined by this method whether the sign of the predominant charge carrier is plus or minus.

Pulsed photoconductivity measurement was applied to the evaporated films because of the impossibility of gaining single crystals sufficiently large to find the sign of the charge carrier and the charge mobility. The evaporation of quaterrylene was made onto a "Mylar" sheet, and then the film was covered with another Mylar sheet. The film thickness was several microns. A short light pulse, approximately a few μsec. long, was applied to the film through the conducting glass electrode, which was held against the back face of one Mylar sheet.** The applied electric field varied from about 1×10^6 V./cm. to 2×10^6 V./cm. The photocurrent was fairly small in comparison with that for anthracene;[6] therefore, a large electric field was necessary in order to obtain photocurrent enough for the detector, a Tektronix oscilloscope, type 545 A. The mobility of the charge carriers was calculated from the $\mu=d^2/Vt$ relation, where μ is the mobility; d, the film thickness; V, the voltage applied and t, the time between the light pulse and the saturation point in the charge pulse. The transit time, t, was very small and comparable to the light pulse duration; therefore, its estimation was rather difficult. The mobility was in the order of 10^{-3} cm^2/V. sec. and was very low in comparison with that of anthracene.[6] The scattering of the charge carriers at the crystalline boundaries in the film specimen may be partly responsible for this low value.

The ionization potential of solid quaterrylene was found from the photoemission

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* When the surfaces of the specimens were in direct contact with air during the preparation of the cell, the photovoltaic behaviour was rather irregular. For example, the glass plate, which was exposed to air after the evaporation of the aluminum electrode (the front-side electrode) on the substrate in a vacuum vessel, was placed in another vessel to make a thin film of the aromatics. After the aromatics had been evaporated, the cell was removed to the former vessel and the electrode(the back-side electrode) was evaporated on the aromatic film. The photovoltaic cell showed a photo-emf. of the same sign when it was illuminated from either side of the electrode. In this case, it was supposed that the contact layer between the aromatics and the back-side electrode was responsible for the induced photo-emf. because the surface of the front electrode was poisoned with air.

* The measurement had to be made in a dark room because it was affected by stray room light.

** The details of the apparatus will be appear elsewhere.

6) R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).

spectrum of the evaporated film. The evaporated film on a glass plate was placed on a centre of a glass vessel, the inner-surface of which had been coated entirely with colloidal graphite as an electron collector, excepting a quartz window for introducing a light. When a monochromatic light was introduced into the vacuum photoemission cell of quaterrylene, a fairly strong photoelectric current was found. The threshold value of its spectral response, as is illustrated in Fig. 8, was around 250 mμ, 4.9 eV.

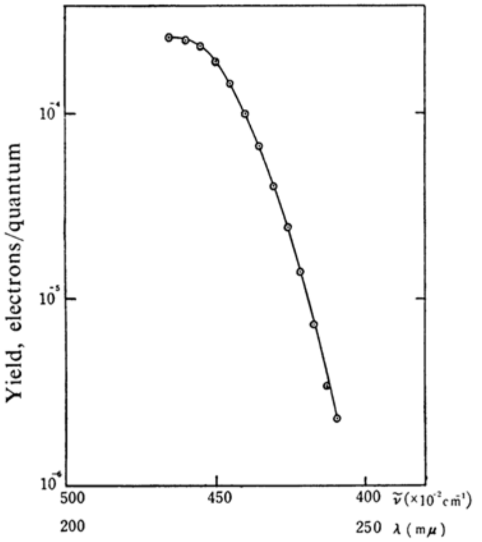

Fig. 8. The quantum yield of the photoemission of quaterrylene.

Discussion

Because the semiconductivity of quaterrylene is fairly high, its numerical values may be employed in further quantitative considerations. This is also true for the photovoltaic effect.

When contact is made between semiconductive material and metal, it is believed that the potential barrier corresponding to the contact potential difference is established. In the case of quaterrylene, such a model was employed to interpret its photovoltaic effect. Supposing the band-type model for the organic semiconductors, the following schematic diagram may be introduced for the system of quaterrylene and aluminium. In the diagram, the band gap, 0.6 eV., is based on the results of the temperature dependence of semiconduction, and the ionization potential, 4.9 eV., is based on the photoemission data. The potential barrier height which is essential for this case is $\Delta\varepsilon/2$ (half of the band gap). When the contact layer is illuminated by a light which has enough energy to excite electrons from the filled band to the conduction band excited electrons are driven to the metal by the electric field which has been built in that layer. (Holes may flow in the opposite direction.) This flow of charge carriers can be detected as photocurrents by the electrometer when the circuit is closed. In the case of an open circuit condition (in the experiment, the insulating resistance of the apparatus was greater than $10^{15}\,\Omega$), the driven carriers accumulate to build a field which prevents the further flow of the carriers. At last, equilibrium is achieved when the Fermi level of quaterrylene is lowered by the amount of the barrier height in dark. Therefore, the photovoltage, which is measured by the electrometer, is the difference between the Fermi level of aluminium and that of quaterrylene, that is, $\Delta\varepsilon/2$.[7] On this basis, the experimental data for photovoltage, 100～300 mV., seemed rather reasonable, since the $\Delta\varepsilon/2$ is about 0.3 eV.

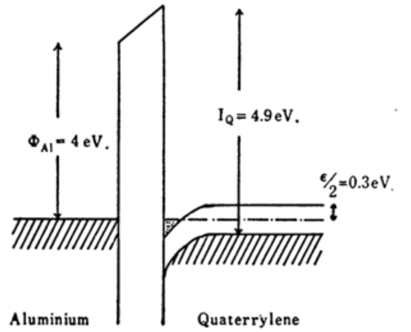

Fig. 9. A schematic energy diagram for the system of quaterrylene in contact with aluminium.

The optical absorption spectra of quaterrylene have several interesting points, and the observation of the polarized light absorption of the single crystals made by the method previously described has been made preliminarily. The work of quantitative assignment is in progress.

Summary

Quaterrylene ($C_{40}H_{20}$) is a dark green-coloured aromatic hydrocarbon and is extraordinarily stable, as it can be heated to over 500°C without decomposition. The semiconduction of the aromatic hydrocarbon possesses a substantial anisotropy by a factor of $10^{7}\sim10^{8}$; the resistivity in the direction parallel to the b axis is $10^{6}\,\Omega$cm. (for a single crystal) or $10^{5}\,\Omega$cm. (for a surface-type cell) and that perpendicular to the b axis is $10^{13}\,\Omega$cm.

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[7] H. Inokuchi, Y. Maruyama and H. Akamatu, This Bulletin, **34**, 1093 (1961).

However, their energy gaps are around 0.6 eV.

From its pulsed photoconduction of the thin film, a drift mobility has been estimated in the order 10^{-3} cm^2/V. sec. However, the rectifying effect of the photoconduction can scarcely be recognized; that is to say, it seems that the mobilities of the holes and electrons in crystal are almost the same.

Further, its photovoltage between aluminium and quaterrylene has a value of 0.1∼0.3 V., while the ionization potential of the hydrocarbon is 4.9 eV. judging from the threshold value of the spectral response of the photoelectric emission.

From these results, a energy level diagram has been introduced for the system of the aromatic hydrocarbon-aluminium contact when a band-type model is employed as the organic semiconductor.

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