820. *Some Physicochemical Properties of Large Aromatic Molecules.*

By N. Parkyns and A. R. Ubbelohde.

Isoviolanthrene (I) and isoviolanthrone (II) have been studied with the object of devising procedures for preparing these and similar substances very pure, in order to characterise their physicochemical properties accurately. Properties investigated include the solubilities in various strong acids, and ultraviolet spectra of solutions in acids of various degrees of dilution. Electrical conductivities of the compressed powdered solids have also been measured, to characterise their activation energies as semiconductors; values characteristic of the pure substances can only be obtained by very careful treatment, since this property appears to be sensitive to the presence of small amounts of related molecules.

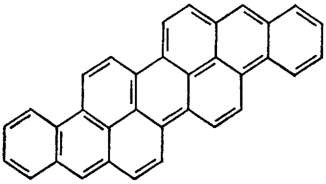
Preliminary observations are recorded on the formation of a new derivative from isoviolanthrene in sulphuric acid.

Quite large polynuclear aromatic molecules are familiar to organic chemists. However, they are very difficult to prepare very pure by conventional methods. Most sublime before they melt at atmospheric pressure, although, with these large molecules, even when the molecular weight is still sufficiently low to permit the use of sublimation at temperatures well below the region where charring of the solid occurs, related impurities often fit into the crystal structure in ways that make ordinary methods of separation ineffective. There are few solvents with boiling point above about 220—250° and in which these large molecules are sufficiently soluble to permit utilisation of differential solubilities of impurities. Interest in certain physicochemical characteristics of such polynuclear aromatic systems has recently grown rapidly.[1-4] Methods of rigorous purification are essential. For example, many of these substances behave as semiconductors whose observed conductivity and even activation energy may depend on the presence of small amounts of impurities in solid solution in the crystals.[4] Again, various physical properties of these large aromatic molecules are particularly interesting as lying between those of small aromatic systems like benzene and very large polynuclear systems like the carbon hexagon networks of graphite. Many such polynuclear aromatic molecules " char " into somewhat

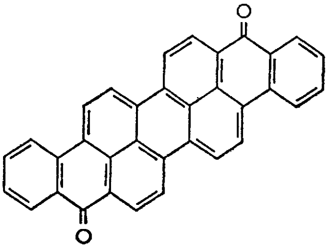
---

[1] Akamatu and Inokuchi, *J. Chem. Phys.*, 1950, **18**, 810.
[2] Inokuchi, *Bull. Chem. Soc. Japan*, 1951, **24**, 222.
[3] Eley and Parfitt, *Trans. Faraday Soc.*, 1953, **49**, 79; 1955, **51**, 1529.
[4] Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 124.

defective graphite or " carbons " by comparatively straightforward bond rearrangements and couplings. In studying the crystal defects of such carbons it would be important to use starting materials which are themselves as free as possible from related impurities, which could otherwise become incorporated as defects in the end product.



(I)



(II)

All these considerations made it desirable to investigate various physicochemical properties of some typical large polynuclear molecules, both on account of their intrinsic interest and with a view to devising more effective methods of purification. Isoviolanthrone (II) was selected as a typical compound of which comparatively large amounts are available commercially. This has probably about the highest molecular weight (456) for which some purification is feasible by sublimation. Isoviolanthrene (I) was prepared from it by the method described below. Various properties investigated for both these molecules included fairly extensive measurements of solubilities in various solvents. Though results with conventional high-boiling substances such as triethanolamine (b. p. 360°) or glycerol (b. p. 290°) proved disappointing, effective use could be made of the findings described below on solubilities in various strong acids, by controlling their water content and the oxidation–reduction conditions. Measurements are also described on the semiconductor properties of the powdered solids. With the purest specimens, the characteristic semiconductor parameters observed differ quite markedly from those of the same substances purified by conventional methods only. These parameters, together with information about the proton affinities of the molecules, are discussed below.

EXPERIMENTAL

Isoviolanthrone (II) was kindly supplied by Imperial Chemical Industries Limited (Dyestuffs Division). It was purified by dissolution in sulphuric acid (98%) and reprecipitation by addition of water,[cf. 6,7] followed by sublimation. When required this starting material was further purified as stated below.

Isoviolanthrene (I) was prepared from the quinone (II) by reduction. The method follows one previously described,[8] but we have found that the ease of reduction is substantially increased by adding a small amount of water. Isoviolanthrone (25 g.), sodium chloride (25 g.), zinc dust (25 g.), and zinc chloride (125 g.) were powdered together in a brass can. Water (12 ml.) was added and the whole mass was gently heated with stirring. Fusion began at about 100° and the heating was increased until the temperature rose to about 200°, where it was maintained for about 20 min. with constant stirring. There was no striking colour change of the melt but the reaction appeared to be practically completed when the original very dark colour of the melt showed tinges of red. The temperature was then raised to about 300° for a few minutes to complete the reaction. After cooling, the black solid was extracted by prolonged boiling with excess of 4N-hydrochloric acid. The residue obtained by filtration was extracted with sodium hydroxide and sodium dithionite solution to which a little pyridine had been added to remove unchanged quinone. Even 0·1% of quinone by weight in this solution gives a deep blue colour; yield 21 g. (84%). Repeated extraction, however, failed to remove the last traces of quinone from the interior of the crystals. When required, further purification was effected as below.

---

[5] Adamson and Blayden, Proceedings of the Third Carbon Conference, Buffalo, 1957, Pergamon, 1959, p. 147.

[6] U.S.P. 1939, 2,180,299.

[7] Russian P. 1939, 56094.

[8] Clar, *Ber.*, 1939, **72**, 1645.

In a variant of the above method, all the constituents were melted together at 200° except the isoviolanthrone which was then added, a gram at a time, with stirring. Towards the end of the reduction the melt became very viscous and the temperature was therefore raised to about 300° for the final additions. Further treatment of the melt was as before, and the yield was about the same.

Removal of most of the unchanged quinone was effected by vacuum sublimation. Ultraviolet absorption spectra of solutions of various fractions in sulphuric acid showed that a higher proportion of quinone was retained in the residue on sublimation. The more volatile fraction after being washed with sodium dithionite solution was therefore sublimed a second time. Sublimation was in all cases effected in the range 400—460°/10^{-5} mm. A simple retort-shaped tube (1 in. diam.) was used; the coherent sublimate collected on the upper walls and there was little or no charring of the residue.

Solubility Tests.—Both compounds (I) and (II) were tested in a preliminary way for solubility in various solvents selected because of their chemical stability and high b. p.s.

FIG. 1. *Spectra of* (A) *isoviolanthrone and* (B) *isoviolanthrene* (*oxidised*) *in* 98% *sulphuric acid.*

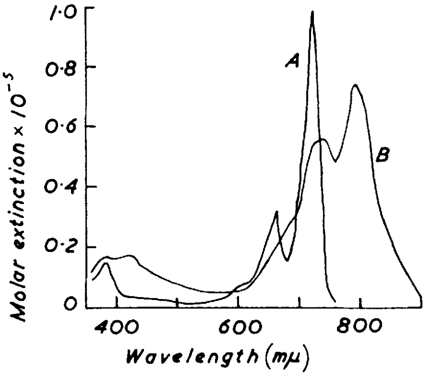
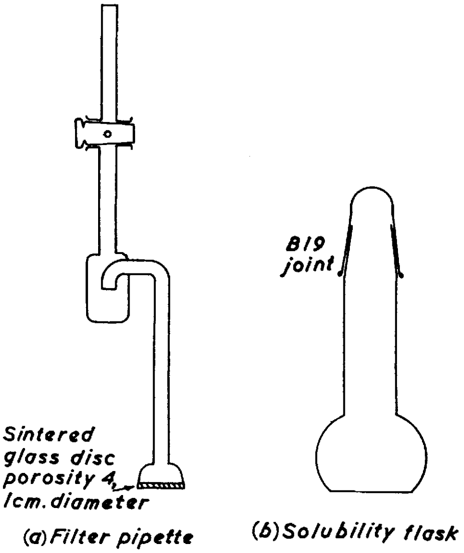


FIG. 2. *Apparatus for solubility determination*; (a) *filter pipette*, (b) *solubility flask.*



However, neither compound was sufficiently soluble in the solvents tried, even at their b. p.s, to make further purification by the method of differential solubilities profitable. In the sequence of solvents, tritolyl phosphate (b. p. 435°), triethanolamine (b. p. 360°), di-(2-methoxyethyl) phthalate (b. p. 350°), diethylene glycol phthalate (b. p. 260°/4 mm.), and dinonyl sebacate (b. p. 224°/0·8 mm.), the highest solubilities were found in tritolyl phosphate and the most marked differentiation in di-(2-methoxyethyl) phthalate.

Both compounds were readily soluble in cold 98% sulphuric acid which gave some promise of practicable further purification. The effects of various strong acids in various concentrations were therefore investigated. In order to characterise these effects, infrared and ultraviolet absorption spectra were measured where appropriate. For infrared spectra, the dry powdered solids were mixed with solid potassium bromide (0·5%) and pelleted. Spectra were recorded on a Hilger H800 continuously-recording infrared spectrometer, and compared with those published by Durie, Lack, and Shannon.[10] Agreement was found within experimental error. A small percentage of either molecule in the other would not be readily detectable in such measurements. For ultraviolet spectra, solutions in concentrated sulphuric acid of controlled concentrations were transferred to stoppered quartz cells 10 mm. thick, care being taken to exclude air and moisture. Spectra were recorded on a Hilger " Uvispek "

---

[9] Bradley and Sutcliffe, *J.*, 1951, 2118.

[10] Durie, Lack, and Shannon, *Australian J. Chem.*, 1957, **10**, 429.

spectrophotometer. Relative heights of the absorption peaks at 790 and 720 mμ were used to estimate the proportions in mixtures of (I) and (II), since the ratio E_{790}/E_{720} is independent of the absolute concentration; E is the extinction coefficient.

The validity of Beer's law in sulphuric acid solutions was verified in the concentration range 10^{-4}M to 10^{-5}M for isoviolanthrone by observation of the extinction coefficients at a series of wavelengths in the range 360—400 mμ, which includes a subsidiary band. Plots of E against molar concentration gave the expected straight lines.

FIG. 3. *Spectra of* (A) *isoviolanthrone,* (B) *isoviolanthrene in methanesulphonic acid, and* (C) *solution* (B) *exposed to air for* 24 *hr.*

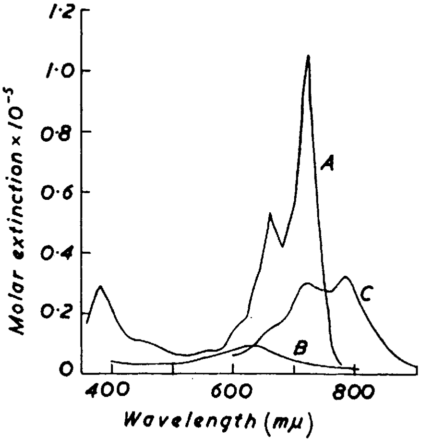


FIG. 4. *Spectra of isoviolanthrone in sulphuric acid of various concentrations:* (A) 90%; (B) 79·2%; (C) 77·2%.

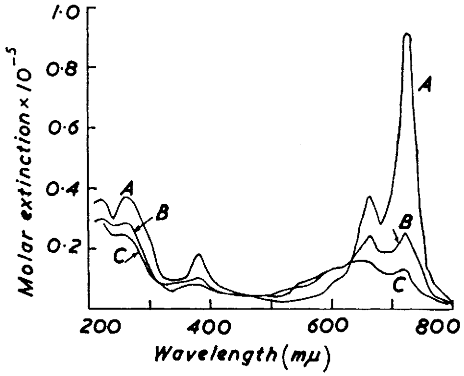
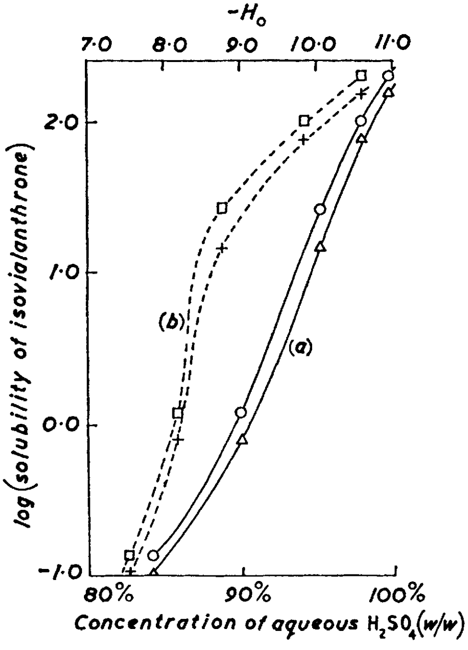


FIG. 5. *Plots of log solubility of isoviolanthrone against* (a) *concentration of sulphuric acid and* (b) *acidity function* $-H_0$: Upper scale □, 40°; +25°. Lower scale ○, 40°; △ 25°.



Effects of Acids.—Isoviolanthrone (II). This dissolved readily in cold 98% sulphuric acid to give a stable turquoise-blue solution and was recovered apparently unchanged by addition of water. This was verified by careful comparisons of the absorption spectra, both ultraviolet and infrared, before and after repeated dissolution in sulphuric acid, precipitation by water, and sublimation. The ultraviolet absorption spectrum is recorded in Fig. 1(*A*). In order to utilise the differential solubility of closely related impurities, measurements were made with the apparatus illustrated in Fig. 2. The long-necked flat-bottomed flask (*b*) was suspended in a thermostat controlled to ±0·1° over the range 25—40°. After addition of isoviolanthrone, various weights of 98% sulphuric acid were added to the flask, and the concentration of acid was varied by adding measured volumes of water through a pipette. By proceeding in this order, instead of directly adding the acid diluted to the end-concentration desired, quicker saturation equilibrium between solid and solution was attained. In measurements of solubilities with these large molecules, whose rate of crystallisation may be quite low, it proved to be essential to verify attainment of the end-concentrations by sucking off small samples of the supernatant solution at intervals by using the filter pipette [Fig. 2(*a*)], and determining the concentrations present. For example, with 84% acid (w/w), equilibrium was effectively attained within 90 hr. at 40°. Since equilibrium is more rapid with stronger acid in which the solubility is higher, 90 hr. was taken as standard time for attainment of equilibrium in determining the solubility curve. To determine the concentration of quinone (II) in the solution sucked off, an aliquot part was diluted with many times its volume of 98% sulphuric acid to a concentration suitable for spectrometric analysis (about 10^{-5}M). The peak in the absorption curve at 720 mμ was used, at which wavelength the extinction for a standard 10^{-5}M-solution of quinone (II) prepared by direct weighing was $E = 0{\cdot}985$.

TABLE. 1 *Effect of strong acids on isoviolanthrene and isoviolanthrone.*

	Isoviolanthrene					
	Cold	Hot	Cold	Hot	Product on adding H_2O	Isoviol-anthrone
Acid	in air		under N_2			
H_2SO_4 (98%)	Dissolves to give blue colour slowly turning green. $\lambda_{max.}$ 790 mμ	Blue colour rapidly turns green	Blue colour much more stable. Very slowly turns green. SO_2 detected	Blue colour rapidly turns green. $\lambda_{max.}$ 790 mμ	Unknown compound (X), contains sulphur, soluble in H_2SO_4. $\lambda_{max.}$ 720 mμ	Dissolves to give turquoise-blue solution. $\lambda_{max.}$ 720 mμ
H_2SO_4 (98%) saturated with $BaSO_4$	Insoluble	Rapidly soluble, giving green solution	—	—	Not examined	Slowly soluble in cold, rapidly in hot to give turquoise-blue solution
$Cl{\cdot}SO_3H$	Rapidly soluble to give green solution	—	—	—	Contained no sulphur. Soluble in H_2SO_4. $\lambda_{max.}$ 720 mμ and 790 mμ (mixture of quinone and hydrocarbon)	Rapidly soluble hot or cold
$F{\cdot}SO_3H$	Rapidly soluble, giving transient blue colour turning green	Soluble, giving green solution			Not examined	Rapidly soluble
$CH_3{\cdot}SO_3H$	Slowly soluble, giving blue colour. Slowly turns turquoise	Rapidly soluble to give blue-green solution	Slowly soluble, giving stable blue solution. $\lambda_{max.}$ 610 mμ	Solution turns green-blue	Unchanged hydrocarbon from cold solution	Soluble, giving blue-green solution. $\lambda_{max.}$ 720 mμ

Fig. 5(*a*) plots the logarithms of solubilities observed for isoviolanthrone in sulphuric acid of various concentrations.

In connection with investigations on isoviolanthrene, described below, preliminary observations were made on solutions of quinone (II) in various other strong acids. These are recorded in Table 2. As far as could be ascertained, pure quinone was always reprecipitated on adding water.

Isoviolanthrene. This dissolves slowly in cold 98% sulphuric acid to give a deep blue solution. If protected by nitrogen (British Oxygen Company " white spot," O_2 <10 p.p.m.), this colour persists for some time, but in air it changes fairly quickly to an olive-green which is stable. The following experiments verified that this change involves an oxidation: (i) Addition of a few drops of hydrogen peroxide (20-vol.) to the blue solution in concentrated sulphuric acid immediately changed it to olive-green. (ii) Bubbling oxygen through a suspension of hydrocarbon (I) in cold sulphuric acid led to rapid dissolution giving the olive-green colour. (iii) Dissolving isoviolanthrene in hot sulphuric acid, either alone or saturated with barium sulphate, gave green solutions directly. (iv) When nitrogen (" white spot ") was bubbled through the blue solution in cold 98% sulphuric acid, sulphur dioxide was formed by reduction of the sulphuric acid and the green colour was produced. For these experiments, 40 mg. of hydrocarbon were dissolved in 50 ml. of cold 98% sulphuric acid and the outgoing gas was passed through 10 ml. of N/100-potassium dichromate. After about 20 min. the blue colour of the acid solution (I) had changed to green, and the dichromate was reduced to the chromium salt. Blank tests showed that there was no transfer of sulphur dioxide in the absence of (I). Similar oxidation of (I) by cold chlorosulphonic acid was also observed in corresponding experiments.

In view of these results with cold concentrated sulphuric acid, the effects of other strong acids on the hydrocarbon (I) were studied. These included sulphuric acid saturated with barium sulphate in order to suppress the concentration of hydrogen ion by virtue of the reaction $H^+ + SO_4^= \rightleftharpoons HSO_4^-$, and chlorosulphonic acid, fluorosulphonic acid, and methanesulphonic acid. Colour change in solution was fairly rapid in all cases, except with methanesulphonic acid. When this acid was carefully protected under nitrogen (" white spot "), stable blue solutions of isoviolanthrene could be obtained. Ultraviolet absorption spectra of these solutions are recorded in Fig. 3(*B*). On dilution with water, the original isoviolanthrene was recovered apparently unchanged. This forms the basis of one process of further purification described below.

Ultraviolet-absorption spectra of the green solution in concentrated sulphuric acid are recorded in Fig. 1(*B*). From these solutions the solid precipitated on addition of water gave evidence of the formation of a new compound (X) apparently by condensation between the sulphuric acid and one or more of the aromatic molecules. Fractional precipitation was carried out by adding water until the acid concentration was 75—85%, and filtering. This precipitated the hydrocarbon and quinone whereas compound X remained in solution, which had a royal-blue colour. On adding more water to the filtrate, to a concentration of about 50%, compound X was precipitated. To purify it from (I) and (II), compound X was redissolved in concentrated sulphuric acid, and refractionated as described, in three successive cycles, until the infrared and ultraviolet absorption spectra showed no further change. Properties of compound X are summarised below, but since it was not directly related to the main objective of the present studies, no complete determination of its molecular size or structure has yet been made.

(*a*) Sodium fusion showed that compound X contained sulphur. No sulphonic acid groups could, however, be detected on boiling with 10% sodium hydroxide solution in which it was completely insoluble.

(*b*) Compound X dissolved in alkaline sodium dithionite solution, suggesting that it contains quinonoid groups.

(*c*) Compound X was practically insoluble in all solvents tried—benzene, xylene, chloroform, ethanol, pentanol, 1-methylnaphthalene, tri-*o*-tolyl phosphate, nitrobenzene, triacetin, acetic acid, " carbowax 350 " (a complex mixture of methylated polyethylene glycols), and dioctyl and dinonyl sebacates. The only exceptions were sulphuric acid, and (to a small extent) boiling glycerol and boiling triethanolamine. This made it impracticable to determine the approximate molecular weight. Its very dilute solution in cold glycerol showed broad absorption bands in the visible spectrum with peaks at 560 and 600 mμ. Its absorption spectrum in 98% sulphuric acid solution is very closely similar to that of isoviolanthrone.

(*d*) Compound X did not melt below 600° but charred progressively above this temperature.

(*e*) Like the ultraviolet absorption spectrum of solutions in sulphuric acid, the infrared absorption spectrum of the solid showed marked similarities to that of isoviolanthrone. Significant differences were observed in the region 1100—1200 cm.$^{-1}$, with wide bands at 1105, 1142, 1210, and 1405 cm.$^{-1}$. These bands were rather diffuse, and very intense, suggesting a condensation product of more than one parent aromatic molecule.

(*f*) In view of what follows, it was noteworthy that the bulk electrical resistance of compound X was extremely low for an organic compound. Pressed pellets showed the resistivity to be $\rho_{20} = 10^7$ ohm cm., with an activation energy of only 0·054 ev.

From solutions of isoviolanthrene in other strong acids tried, a mixture of hydrocarbon and quinone was recovered on adding water, as recorded in Table 1.

Methods of Further Purification of Isoviolanthrone and Isoviolanthrene.—On the basis of studies summarised above, definitive methods used for further purification were as follows:

(1) *Isoviolanthrene.* This was first produced by reduction of the quinone and the reaction mixture was extracted with 4N-hydrochloric acid to remove the bulk of inorganic impurities. The crude hydrocarbon was boiled with alkaline dithionite–pyridine solution (3 or 4 times) until the bulk of quinone was removed. Two sublimations then yielded substantially pure material. Further purification was by treatment with cold methanesulphonic acid and water as explained below, followed by final sublimation.

(2) *Isoviolanthrone.* As obtained from Imperial Chemical Industries Limited (Dyestuffs) this was fairly pure and could be dissolved directly in 98% sulphuric acid, followed by filtration and reprecipitation by reducing the acid concentration to about 90%. Sublimation then yielded a pure product.

Electronic Properties of (I) *and* (II).—Certain electronic properties of these solid polynuclear aromatic molecules are sensitive to the presence of impurities in solid solution. To test the recommended procedures, the electrical conductivity of the solids was compared (i) when they were prepared by conventional purification and (ii) when further purified as described. To survey the range of possibilities, actual solids used included:

Hydrocarbon I(i), purified by repeated sublimation and washing with alkaline dithionite solution until test was no longer positive (boiling a small sample with alkaline sodium dithionite solution containing a little added pyridine). Sublimation was always the last step.

I(ii) was prepared from I(i) further purified by agitation with cold concentrated methanesulphonic acid protected by oxygen-free nitrogen. Tests showed that the acid-soluble fraction contained a little quinone, but that the insoluble portion was free from quinone.

Quinone II(i), sublimed from the crude material.

II(ii), purified by acid treatment as described, followed by sublimation.

II(iii), which was the same as quinone II(ii) except that known amounts of benzanthrone had been added as impurity; *e.g.*, 0·1 mole % of benzanthrone was added to the powdered quinone II(ii), and the whole dissolved in cold concentrated sulphuric acid to assist incorporation; it was completely reprecipitated by adding water and sublimed.

Pure benzanthrone was also studied as reference material and was purified as for isoviolanthrone.

Difficulties in measuring the electrical conductivity of powders are well known, because of the effect of the applied pressure on the contact electrical resistances in polycrystalline material. For the present purpose of comparing closely similar materials, a procedure giving definite and characteristic values was aimed at. Other work [11] suggested that much of the difficulty could be obviated by promoting plastic flow under pressure to increase contact areas between crystals. It was found that reproducible results could be conveniently obtained with the present materials by forming a pellet of approx. 0·5 cm. diameter in a screw pellet press, and heating the pellet for 3 hr. to release strain energy by plastic flow whilst the screw pressure was applied. Heating was at 100° for (II) and at 300° for (I). Check experiments with heating under dry nitrogen gave the same result. Indirect methods showed that the screw press used exerted about 300 kg./cm.^{2}. On release of the screw, the pellet expands somewhat; further heating at 100° for a few hours releases any remaining strain energy sufficiently to yield steady and reproducible values of the resistance, R. In contrast with measurements on the powders, dR/dP in these pellets is zero, within the range 0—10 kg./cm.^{2}.

Other workers [12,3] have used static pressures up to about 80 kg./cm.^{2} without any annealing. This implies using solids with considerable strain energy at contact points between crystals, though their values show the convenient property that dR/dP is small above this order of pressures. By our annealing procedure, dR/dP becomes negligible at much lower pressures,

---

[11] Lewis, Orr, and Ubbelohde, *Proc. Phys. Soc.*, 1958, *B*, **70**, 928.

[12] Inokuchi, *Bull. Chem. Soc. Japan*, 1955, **28**, 570.

which seems more satisfactory for purposes of characterisation by means of comparative measurements. With materials of such high resistance, various other complications have to be kept in view. On applying a D.C. voltage gradient, the end value of resistance was found to lie above the initial value by a factor which might be as high as 20 or 30. Our values all refer to asymptotic end-results reached after about 30 minutes' application of voltage.

A.C. has also been used in place of D.C., with the aim of eliminating contact effects.[13,3] A D.C. method was preferred for compounds of such high resistance as those now studied. The slow relaxation processes that are evident when D.C. is used could introduce frequency-dependent terms with A.C.

To measure the resistance at various temperatures a simple cell of silica was used, similar in design to that previously described.[14] The sample was in series with a standard resistor of high known value and the potential drop across this was measured on an electrometer (Electronics Instrument Limited, Vibron type 33c). This enabled the voltage gradient to be kept below 100 v/cm. and avoided non-ohmic effects. Tests showed that Ohm's law was obeyed up to about 500 v/cm. An air-bath controlled to ±0·5° was used for temperature control. This consisted of a copper can 6 in. high and 4 in. in diameter around which was wound a 100-ohm. heater in 4 separate strips each being 1 in. wide; heat-resisting cement covered the outside of the heating wire. Temperature was controlled by two variable resistors in series with the heater. Because the heating current was D.C., switching was effected by a vacuum switch which in turn was actuated by a relay from an Airmec N241 temperature controller. The whole apparatus was electrically and magnetically screened by being placed in a large soft-iron can.

Plots of log ρ against $1/T$, where ρ is the resistivity, give straight lines at 30—140° (see Fig. 6). Calculated parameters from closest fit of the equation log $\rho/\rho_0 = \varepsilon/kT$ to experimental data are given in Table 2. Some authors [2-4] use an alternative equation with an energy gap $\Delta\varepsilon$ twice our value of ε.

An alternative method of incorporation was tested to verify whether dissolution in sulphuric acid and complete reprecipitation to produce II(ii) might have caused the marked changes recorded in Table 2 on further purification of isoviolanthrone. These are illustrated in Fig. 6. Benzanthrone (1%) was mixed with the isoviolanthrone in a ball mill, and a pellet was made from the mixture. Measurements were first made before annealing at high temperature. The log ρ–$1/T$ plot consists of two intersecting straight lines of slope $\varepsilon = 0·75$ ev and $\varepsilon = 1·30$ ev at lower and higher temperatures, respectively. This corresponds to simple summation of the conductance properties of the pure components. A similar result was noted for a 0·1% mixture (Fig. 6*x*). However, on annealing this sample in the usual way at 300°, a result exactly comparable with that of [II(i)] was obtained, with $\varepsilon = 0·52$ ev, $\rho_{20} = 3·6 \times 10^{11}$ ohm cm., indicating that both methods of incorporation eventually lead to the same plot, corresponding with impure isoviolanthrone (Fig. 6*y*).

TABLE 2. *Effects of impurities on semiconductor characteristics of aromatic hydrocarbons* (II) *and quinones* (I).

Sample	ε (ev)	ρ_{20} units (10^{11} ohm cm.)	ρ_0 (ohm cm.)	Sample	ε (ev)	ρ_{20} units (10^{11} ohm cm.)	ρ_0 (ohm cm.)
I(i)	0·74	2100	20	II(ii)	0·66	2200	800
I(ii)	0·81	3600	6·3		0·65	1200	630
II(i)	0·53	4·0	320		0·74	6000	150
	0·50	17	4000	II(iii)	0·49	0·12	50
	0·48	2·5	1600		0·56	170	4800

With pure benzanthrone, resistances were too high to permit good reproducibility. At temperatures above 80°, two different pellets had the parameters:

$$\varepsilon = 1·71 \text{ ev}, \ \rho_{100} = 1·6 \times 10^{16} \text{ ohm cm.}, \ \rho_0 = 1·6 \times 10^{-7} \text{ ohm cm.}$$

$$\varepsilon = 1·35 \text{ ev}, \ \rho_{100} = 4·3 \times 10^{15} \text{ ohm cm.}, \ \rho_0 = 3·5 \times 10^{-3} \text{ ohm cm.}$$

In view of the scatter of the points caused by the very high resistance to be measured, these values of ε can be regarded as in fair agreement with the value of $\varepsilon = 1·30$ ev obtained at

---

[13] Koops, *Phys. Rev.*, 1951, **83**, 121.

[14] Slough and Ubbelohde, *J.*, 1957, 982.

higher temperatures from mixtures of isoviolanthrone and benzanthrone, before annealing [cf. Fig. 6(*b*)].

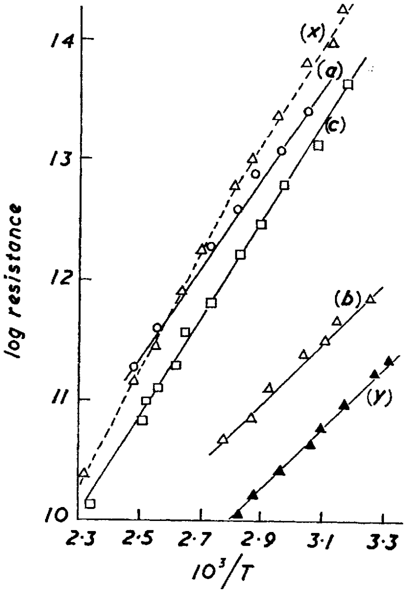


FIG. 6. *Plots of log resistance against* $1/T$ *for pure and impure samples*: (x) Isoviolanthrone–benzanthrone (0·1%). (a) Pure isoviolanthrone II(ii). (b) Impure isoviolanthrone II(i). (c) Pure isoviolanthrone I(ii). (y) Same as (x) after annealing.

DISCUSSION

One primary effect of acids in facilitating dissolution of a polynuclear compound R is through the formation of a proton adduct RH^+ from the neutral molecule. This proton adduct RH^+ is much more soluble in a strongly ionising medium such as concentrated sulphuric acid than is the parent molecule. Such dissolution is reversed on dilution with water, the original compound usually being recovered. Aromatic molecules of different structures can have very different proton affinities in this respect, and in the absence of other complications this makes purification by acid treatment a good selective method. Various acids with differing acidity functions can be used, and the acidity can be controlled by adding water or soluble sulphates. Another more chemical effect whereby strong acids can increase the solubility of R is by increasing the proportion of polar groups in the molecules, for example, by sulphonation or by oxidation. Whereas sulphonation may be reversible, oxidation usually is not. However, both effects are undesirable in purifying large polynuclear molecules and the use of acids should if possible be avoided if intervention of such processes is suspected.

Combined with previous information,[16,18] the experimental evidence presented above is consistent with the view that isoviolanthrone R^1 dissolves in strong acids to give a reversible proton adduct in the way suggested. This can be represented by the equation

$$R^1 + H^+ \rightleftharpoons R^1H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Isoviolanthrene also probably dissolves initially to form a proton adduct:

$$R^2 + H^+ \rightleftharpoons R^2H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In methanesulphonic acid, reaction stops at this stage but under oxidising conditions the further reaction occurs: [15]

$$R^2H^+ \longrightarrow H^+ + (R^2)^{++} + 2e \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

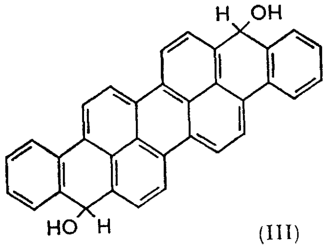
When the proton concentration is repressed, *e.g.*, by adding barium sulphate, formation of $(R^2)^{++}$ in solution probably occurs directly by oxidation of the solid. On these views,

[15] Van der Meij, Thesis, Amsterdam, 1958.

[16] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 271.

the observed solubility of isoviolanthrone in sulphuric acid might depend on the acidity function[16] H_0. Plots to test this by using known acidity functions are shown in Fig. 5(*b*). No simple interpretation giving a relation between H_0 and total solubility m_S has been found that does not contain a term in log m_R, where m_R is the concentration of the un-ionised quinone in solution. In the absence of further experimental information, m_R remains an essentially indeterminate quality.

From the absorption spectra of the quinone in varying concentrations of acid, calculations of the basicity constant pK_B could in principle be made. Unfortunately, in the region of acid concentration between 72 and 78%, where the spectrum of the un-ionised quinone makes an appreciable contribution, the solubility of the isoviolanthrone becomes vanishingly small, so that direct accurate determinations of absorption spectra were impossible. An estimate by using the calculation due to Hammett and his colleagues[17] gave $pK_B = -7{\cdot}3$. On this basis isoviolanthrone appears to have approximately the same basicity and hence delocalisation energy as anthraquinone.[18] Only preliminary quantum-mechanical calculations are yet available for isoviolanthrene[19] and none for isoviolanthrone.



(III)

On addition of water to the strongly acid solutions the quinone is recovered unchanged by reversal of reaction (1). In one instance the hydrocarbon is likewise recovered by reversal of reaction (2). In the oxidised solutions of hydrocarbon a mixture of quinone and hydrocarbon appears to be present; this is probably formed by disproportionation of some intermediate (III).

The sequence of reactions might be

$$(R^2)^{++} + 2OH^- \longrightarrow (III)$$
$$2(III) \longrightarrow R^2 + R^1 \text{ (disproportionation)}$$

In concentrated sulphuric acid some compound X is also found.

The effect of impurities is very evident from measurements on the electrical conductivity. Some discussion about their mode of action has been presented for smaller polyacenes.[4] In considering our present results for isoviolanthrene, its ready oxidisability must be kept in mind. ε for the pure hydrocarbon is unlikely to lie below 0·81 ev. Sample I(i) gave $\varepsilon = 0{\cdot}74$ ev. Possibly this contained a trace of quinone, although the difference may not be experimentally significant. The resistance at 20° agrees well with previous published data,[2] but the activation energy is almost twice that of the former work (0·41 ev). It is of interest that, on the basis of Northrop and Simpson's postulate that activation energy is related to the height of the first triplet state, our value of 0·81 ev agrees far better with a straight-line plot of ε against the energy gap between ground state and triplet state of the molecule, than do the quoted values of Inokuchi.[2]

It would seem from the present results that benzanthrone may have been present in samples of isoviolanthrone previously studied,[2] since the activation energies reported lay around 0·40 ev with ρ_{20} around 10^8 ohm cm. By comparison with the results of Northrop and Simpson,[4] samples with activation energy 0·65 ev as now obtained (Table 2) would appear to have had the concentration of impurity reduced to less than about 5×10^{-4}M. By successive dilutions of the isoviolanthrone II(iii) treated with benzanthrone, by pure isoviolanthrone II(ii) it is found that the conductance parameters are affected by the added impurity down to at least 10^{-5}M.

Dept. of Chemical Engineering and Chemical Technology,
Imperial College of Science and Technology,
London, S.W.7.

[*Received, November 3rd*, 1959.]

---

[17] Flexser, Hammett, and Dingwall, *J. Amer. Chem. Soc.*, 1935, **57**, 2103.
[18] Macker, Hofstra, and van der Waals, *Trans. Faraday Soc.*, 1958, **54**, 66.
[19] B. Pullman, Proceedings of the Third Carbon Conference, Buffalo, 1957, Pergamon, 1959, p. 3.