
QUARTERLY REVIEWS

SEMICONDUCTIVITY OF THE PHTHALOCYANINES

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1. Scope

WITHIN the last few years a number of Reviews¹ and Symposia² have been devoted to the discussion of the electrical conductivity of organic molecules. Of the organic semiconductors, the phthalocyanines excite particular interest since they were some of the first organic materials found to display intrinsic semiconductor properties. The present Review is concerned with the phthalocyanines, the phthalocyanine polymers and the corresponding thermal activation energies for conduction.

2. Phthalocyanines

Several excellent Reviews on phthalocyanine chemistry are available. These discussions range from brief, lucid, and authoritative introductions³ to a number of more specialized works.⁴

The metal phthalocyanines are formed by a vigorous reaction initiated by the heating of a metal, or metal salt, with aromatic *ortho*-dinitriles or related substances. Phthalocyanines are related to porphyrin, the fundamental nucleus of chlorophyll and of hæmoglobin. The phthalocyanine nucleus, an azaporphyrin, may be derived from the parent porphyrin nucleus by replacement of the methine groups by nitrogen atoms. The two hydrogen atoms attached to the central nitrogen atoms of the phthalocyanine

¹ (a) Eley, *Research*, 1959, 12, 293; (b) Garrett, "Semiconductors," ed. Hannay, Reinhold Publ. Corp., New York, 1959; (c) Inokuchi and Akamatu, "Solid State Physics," ed. Seitz and Turnbull, Academic Press, New York, 1961, Vol. XII; (d) Boldebeck, "Organic Semiconductors; Literature Survey," Report No. 56-RL-1490, General Electric Co., U.S.A., 1956; (e) Brown and Aftergut, "Investigation of Organic Semiconductors," Report No. 59-469, General Electric Co., U.S.A., 1959.

² "Proceedings of the Princeton University Conference on Semiconduction in Molecular Solids," ed. Pohl, Ivy-Curtis Press, Philadelphia, 1960; "Symposium on Electrical Conductivity in Organic Solids," eds. Kallmann and Silver, Interscience Publ. Inc., New York, 1961; "Organic Semiconductors," eds. Brophy and Buttrey, Macmillan, New York, 1962.

³ (a) Dahler, *Ind. Eng. Chem.*, 1939, 31, 839; (b) Linstead, "Thorpe's Dictionary of Applied Chemistry," 4th edn., Longmans, Green and Co., London, 1949, Vol. IX, pp. 617—620; (c) Johnson, "Encyclopedia of Chemical Technology," eds. Kirk and Othmer, Interscience, New York, 1953, Vol. X, pp. 607—611.

⁴ (a) Venkataraman, "The Chemistry of Synthetic Dyes," Academic Press, New York, 1952, Vol. II, pp. 1118—1142; (b) Robertson, "Organic Crystals and Molecules," Cornell University Press, Ithaca, New York, 1953; (c) Lubs, "The Chemistry of Synthetic Dyes and Pigments," Reinhold Publ. Corp., New York, 1955, pp. 577—624; (d) Gerstner, "Die Chemie der Applikation von Komplexfarbstoffen," Akademie-Verlag, Berlin, 1959, pp. 187—195.

cyanine molecule are replaceable by various metals. The phthalocyanine molecule is rigidly coplanar and tetradentate, with the four co-ordinating nitrogen atoms occupying the corners of a square. All the carbon–nitrogen bonds within the large 16-membered central ring are, to within a few hundredths of an Angström, approximately equal. In metal-free phthalocyanine, the carbon–nitrogen distance is 1.34 Å and in nickel phthalocyanine the distance is 1.38 Å^{4b}. Detailed studies of the geometrical configurations of the phthalocyanines can be found elsewhere.^{4b,5}

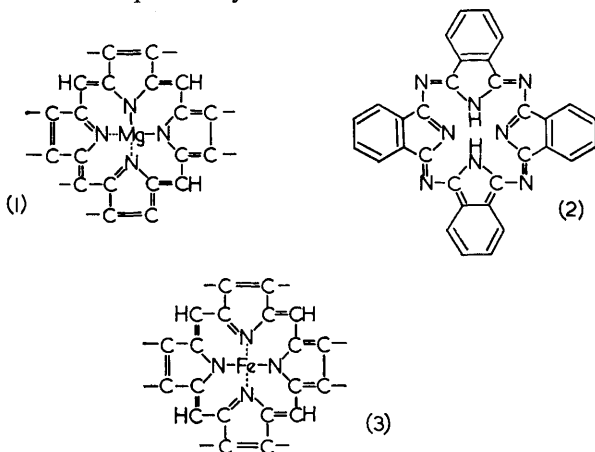


FIG. 1. Porphyrin ring structures; (I) chlorophyll nucleus; (II) phthalocyanine; (III) hemoglobin nucleus.

The existence of three polymorphic forms of phthalocyanine, α , β , and γ , is supported by *X*-ray⁶ and infrared⁷ studies. Of the three forms, the β is the most stable. Heating the other forms to 300° converts them to the β -form. With few exceptions, all electrical measurements of the phthalocyanines have been made on the β -crystal form.

3. Phthalocyanine Polymers

The phthalocyanine unit has been polymerised and, except for a few cases, the polymerisations were made in attempts to prepare dyes, dielectric films, or materials having a high thermal stability. Because of the difficulties encountered in the isolation, purification, and identification of the phthalocyanine polymers, interest in their conducting properties has been somewhat limited.^{8,9,10}

⁵ Barrett, Dent, and Lindstead, *J.*, 1936, 1719.

⁶ (a) Susich, *Analyt. Chem.*, 1950, 22, 426; (b) Karasek and Decius, *J. Amer. Chem. Soc.*, 1952, 74, 4716.

⁷ (a) Ebert and Gottlieb, *J. Amer. Chem. Soc.*, 1952, 74, 2806; (b) Sidorov and Kotlyar, *Optika i Spektroskopiya*, 1961, 11, 175.

⁸ Epstein and Wildi, *J. Chem. Phys.*, 1960, 32, 324.

⁹ Lawton and McRitchie, "Research on Thermostable Molecules and Polymers," Report No. 57-642, Battelle Memorial Institute, Columbus, Ohio, 1957.

¹⁰ Felmayer and Wolf, *J. Electrochem. Soc.*, 1958, 105, 141.

(a) **Dimers and Trimers.**—Co-condensation of 3,3',4,4'-tetracyanodiphenyl ether and phthalonitrile with copper-bronze results in the formation of a product in which polymerisation proceeds no further than the dimeric or trimeric stage.¹¹ A dimer of copper phthalocyanine is obtained by the reaction of pyromellitic dianhydride with phthalic anhydride.⁹ The extent of polymerisation of this material was estimated from probability considerations based on the ratio of reactants.

(b) **Linear Polymers.**—Linear polymeric phthalocyanines are prepared by reacting phthalic anhydride and a copper salt with either pyromellitic acid or 3,3',4,4'-tetracarboxydiphenyl ether in a flux of urea.¹² In both reactions, the linear polymers obtained are soluble in solvents in which copper phthalocyanine monomer and planar polymers of phthalocyanine exhibit little or no solubility. Some linear polymers have been estimated to contain 7—8 phthalocyanine units.^{12a}

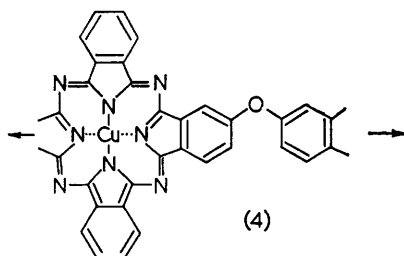


FIG. 2. Expected repeating unit of a linear polymeric copper phthalocyanine from phthalonitrile, 3,3',4,4'-tetracyanodiphenyl ether and copper (ref. 11).

(c) **Planar Polymers.**—The majority of the phthalocyanine polymers are extensions of the monomeric unit in two dimensions. These polymers are insoluble in organic solvents but are soluble in concentrated sulphuric acid. Reaction of a metal, or metal salt, and urea with pyromellitic acid,¹⁰ pyromellitic dianhydride,¹³ or with pyromellitonitrile⁸ yields planar polymers consisting of an estimated 10 units, 3—34 units, and 5 units, respectively. A completely cross-linked copper phthalocyanine polymer is obtained from the reaction of phthalic anhydride, pyromellitic dianhydride, urea and copper chloride.⁹ Using starting materials of higher molecular weights, it is possible to synthesise other planar polymers of phthalocyanine. Planar-type polymeric copper phthalocyanines are prepared by heating 3,3',4,4'-tetracyanobiphenyl or biphenyl-3,3',4,4'-tetracarboxylic acid with urea and a source of copper in the presence of a catalyst.¹⁴

¹¹ Marvel and Martin, *J. Amer. Chem. Soc.*, 1958, **80**, 6600.

¹² (a) Rassweiler, "Polymeric Phthalocyanines," *Diss. Abs.*, 1958, **18**, 403; (b) Marvel and Rassweiler, *J. Amer. Chem. Soc.*, 1958, **80**, 1197.

¹³ Drinkard, "Studies on the Oxidative and Thermal Stability of Complex Inorganic Compounds," *Diss. Abs.*, 1957, **17**, 499.

¹⁴ "High Temperature Dielectric Film," Final Report for Contract DA 36-039-sc-87, Sprague Electric Co., North Adams, Mass., U.S.A., 1952.

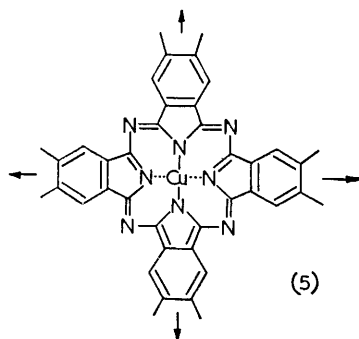


FIG. 3. Expected repeating unit of a planar polymeric copper phthalocyanine from pyromellitonitrile, urea and cuprous chloride (ref. 8).

4. Conductivity of the Phthalocyanines

In 1948, Eley¹⁵ and Vartanyan¹⁶ independently discovered that the phthalocyanines had a lower electrical resistivity than most organic substances. The resistivity, ρ , of a phthalocyanine is a function of the temperature and is expressed by the equation

$$\rho = \rho_0 \exp(E/kT) \quad (1)$$

Equation (1) is typical of semiconducting materials possessing a thermal activation energy, E , for conduction. Although eqn. (1) represents the experimental data, a detailed interpretation of the equation is not simple. Electrical conductivity of molecular crystals greatly depends on both the molecular and the intermolecular barriers. Hence, the thermal activation energy appears to be a composite of both these effects.⁸ In general, the thermal activation energy can be related to the energy necessary for the production of charge carriers in the molecule. The number of carriers is proportional to $\exp(-\epsilon/2kT)$ provided conduction is related to the mobile electrons which have been promoted to a level of energy greater, by the energy interval ϵ , than the lower bound energy level. The approximate formula for the conductivity, σ , can be written as

$$\sigma = \sigma_0 \exp(-\epsilon/2kT) \quad (2)$$

or in terms of the resistivity

$$\rho = \rho_0 \exp(\epsilon/2kT) \quad (3)$$

By convention, the energy interval, ϵ , is used instead of the activation energy, E , because it is somewhat analogous to the energy gap of the familiar band theory model for inorganic semiconductors.

Because of the relatively little knowledge available on the intermolecular interactions in molecular crystals, it is difficult to formulate a suitable

¹⁵ Eley, *Nature*, 1948, **162**, 819.

¹⁶ Vartanyan, *Zhur. fiz. Khim.*, 1948, **22**, 769.

mechanism for the electronic conduction in organic solids. Inokuchi and Akamatu¹⁶ present a brief but valuable summary of the proposed theories for the mechanism of charge transfer between molecules, and discuss the interpretation of the activation energy, E , in the empirical eqn. (1) according to the various concepts. Of these theories, only that of Eley and his co-workers¹⁷ will be outlined in this Review.

According to Eley the conductivity and the energy interval may be regarded as being associated with the mobile π -electrons of the conjugated ring structure of the phthalocyanines^{1a} since substitution of the two central hydrogen atoms by various metals has little effect on the electrical conductivity and the magnitude of the energy interval.¹⁸ The π -electrons form an "electron gas" which may be envisaged as a cloud stretching along the carbon-nitrogen-carbon ring both above and below the plane of the phthalocyanine molecule.

In the normal state, each of the lower energy levels will be filled by two electrons, the highest occupied level being determined by the number of electrons that are available. All higher energy levels will be empty. For conduction to occur in the phthalocyanine molecule, a π -electron must be thermally or optically excited from the highest filled energy level to the lowest unfilled energy level.¹⁷ If n is the number of π -electrons constituting the "gas", the normal state has $n/2$ lower energy levels, each containing two electrons. Conduction is associated with the transfer of electrons from the highest occupied level, $n/2$, to the lowest unoccupied level, $n/2 + 1$. These two levels are separated by ϵ , the energy interval.

The magnitude of the energy interval has been estimated¹⁷ using a treatment similar to that proposed by Kuhn¹⁹ for computing the light absorption of organic dyes. It is possible, using certain simplifications, to consider the mobile π -electrons of a conjugated path as electrons in a one-dimensional box and, using the Schrödinger equation, to calculate the energy values for a particular π -electron. In molecules where the π -electrons form an open path, the energy interval, ϵ , is

$$\epsilon = \frac{h^2 (n + 1)}{8 m l^2} \quad (4)$$

and, for a closed path,

$$\epsilon = \frac{h^2 n}{4 m l^2} \quad (5)$$

where h is Planck's constant, n , the total number of π -electrons in the path considered, m , the mass of the electron, and l , the total path length. Since the average carbon-nitrogen distance in the phthalocyanines is 1.36 Å, the plot in Fig. 4 of eqns. (4) and (5) was made using $1.36n$ for l , the path length.

¹⁷ (a) Eley, Parfitt, Perry, and Taysum, *Trans. Faraday Soc.*, 1953, **49**, 79; (b) Eley and Parfitt, *Trans. Faraday Soc.*, 1955, **51**, 1529.

¹⁸ Fielding and Gutman, *J. Chem. Phys.*, 1957, **26**, 411.

¹⁹ Khun, *J. Chem. Phys.*, 1949, **17**, 1198.

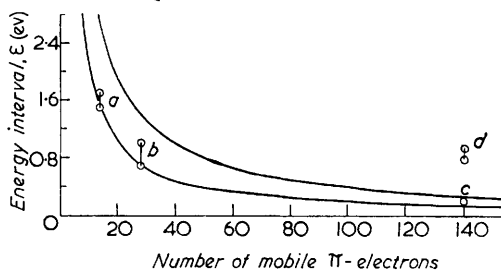


FIG. 4. Experimental ϵ values and the Eley equations (after Eley).

The curves A and B are calculated by means of eqns. (4) and (5) respectively. References: ^a Eley, *Research*, 1959, **12**, 293; ^b Lawton and McRitchie, "Research on Thermostable Molecules and Polymers," Report No. 57-642, Battelle Memorial Institute, Columbus, Ohio, 1957; ^c Epstein and Wildi, *J. Chem. Phys.*, 1960, **32**, 324; ^d Fel-mayer and Wolf, *J. Electrochem. Soc.*, 1958, **105**, 141.

Although eqns. (4) and (5) appear to be simple, they must be used with utmost caution since n , the number of mobile π -electrons, is not necessarily the same as the total number of π -electrons in the molecule^{1a,17}. To use the equations, some guide to the values of n and l is required. A value of l for the phthalocyanine molecule has been obtained by Lonsdale²⁰ from the anisotropy of the diamagnetic susceptibility, and from this value it is possible to infer the magnitude of n . Lonsdale's method gives a value of 18.8 Å for l , which is the circumference of the large central closed ring, with the number of mobile π -electrons, n , equal to 14.

This discussion of the conduction mechanism for the phthalocyanines has been restricted to the single molecule with no reference to the intermolecular conduction process. On the molecular level, highly conjugated molecules, such as phthalocyanines and aromatic hydrocarbons, may be regarded as excellent conductors since there is no dissipation mechanism to impede the electron flow around the molecular ring.^{1b} Apparently, the actual limiting steps in the bulk conduction process are the transfer of electrons from crystal to crystal and the mobility of the electrons from one molecule to the next.

Values of the energy interval, ϵ , obtained for various phthalocyanines are listed in Table 1. The discrepancy of the ϵ value for a given phthalocyanine can be attributed to the sample purity and the measurement technique. Eley has attributed the higher energy interval values of his earlier measurements¹⁵ to the intercrystalline resistance of the lightly packed phthalocyanine powders,^{1a} and his more recent measurements were made using compacted samples to minimise this factor.^{17b} Since most of the resistivity measurements of the phthalocyanines are made on compacted powders, efforts are made to reduce the intercrystalline resistance by using compressed samples. The resistivity of compacted phthalocyanine powders does not change appreciably after pressures of 80 kg. cm.⁻² are reached^{17a} and it has been tacitly assumed that this limiting value is the true resistivity of the material.^{1a}

²⁰ Lonsdale, *Proc. Roy. Soc.*, 1937, *A*, **159**, 149.

TABLE 1. *Energy interval values, ϵ , of monomer phthalocyanines*

ϵ (ev)	Sample form	Temp. range	Atm.	Ref.
Metal-free phthalocyanine				
2.39	lightly packed crystals	300—470°	H ₂	<i>a</i>
0.87	film rubbed on quartz	10—100	vac.	<i>b</i>
0.90	film rubbed on quartz	10—100	some O ₂	<i>b</i>
2.39	lightly packed crystals	300—500	H ₂ ; N ₂	<i>c</i>
1.1	compact, 80 kg./cm. ²	300—500	H ₂ ; N ₂	<i>c</i>
1.44—1.87	single cryst.; subl. film	25—160		<i>d</i>
1.40—2.0	single cryst.; film	25—420	He	<i>e</i>
1.49	compact, 0.5 kg./cm. ²	150—350	vac.	<i>f</i>
1.73	film		O ₂ -free	<i>g</i>
1.3	subl. film		vac.	<i>h</i>
1.71	single crystal	50—390	N ₂	<i>i</i>
1.8	compact, 80 kg./cm. ²	200—350	N ₂	<i>j</i>
1.50—1.7	(summary of measurements)			<i>k</i>
0.5	compact, α -form	60—170	N ₂	<i>j</i>
Copper phthalocyanine				
2.6	lightly packed crystals	300—470	H ₂	<i>a</i>
1.2	film rubbed on quartz	10—100	vac.	<i>b</i>
0.82	film rubbed on quartz	10—100	some O ₂	<i>b</i>
1.85	single cryst.; subl. film	25—160		<i>d</i>
2.1	lightly packed crystals	300—500	H ₂ ; N ₂	<i>c</i>
1.2	subl. film		vac.	<i>h</i>
1.64	film		O ₂ -free	<i>g</i>
1.64	single crystal	50—390	N ₂	<i>i</i>
1.79	lightly packed crystals	25—340	N ₂	<i>l</i>
Copper phthalocyanine, chlorinated				
1.86	lightly packed crystals		N ₂	<i>l</i>
Nickel phthalocyanine				
1.60	single crystal	50—390	N ₂	<i>i</i>
Cobalt phthalocyanine				
1.60	single crystal	50—390	N ₂	<i>i</i>
Platinum phthalocyanine				
1.52	lightly packed crystals		N ₂	<i>l</i>

TABLE 1.—*continued*

ϵ (ev)	Sample form	Temp. range	Atm.	Ref.
Magnesium phthalocyanine				
0.78	film rubbed on quartz	10—100	vac.	<i>b</i>
0.47	film rubbed on quartz	10—100	some O ₂	<i>b</i>
1.2	film; subl. film			<i>g</i>
Zinc phthalocyanine				
1.51	film		O ₂ -free	<i>g</i>

^a Eley, *Nature*, 1948, **162**, 819; ^b Vartanyan, *Zhur. fiz. Khim.*, 1948, **22**, 769; ^c Eley, Parfitt, Perry, and Taysum, *Trans. Faraday Soc.*, 1953, **49**, 79; ^d Kleitman, "Electrical Properties of Phthalocyanines," Report PB 111,419, U.S. Dept. of Commerce, Office of Tech. Service, Washington, 1953; ^e Kleitman and Goldsmith, *Phys. Rev.*, 1954, **98**, 1544; ^f Eley and Parfitt, *Trans. Faraday Soc.*, 1955, **51**, 1529; ^g Vartanyan and Karpovich, *Doklady Akad. Nauk. S.S.S.R.*, 1956, **111**, 561; ^h Baba, Chitoku, and Nitta, *Hokkaidô Daigaku Ôyô Denki Kenkyûjo Iho*, 1956, **8**, 127, (*Chem. Abs.*, 1957, **51**, 9297f); ⁱ Fielding and Gutman, *J. Chem. Phys.*, 1957, **26**, 411; ^j Wihksne and Newkirk, *J. Chem. Phys.*, 1961, **34**, 2184; ^k Eley, *Research*, 1959, **12**, 293; ^l Felmayer and Wolf, *J. Electrochem. Soc.*, 1958, **105**, 141.

Vartanyan has withdrawn the ϵ values which he first reported,¹⁶ on the basis that the films contained oxygen impurities.²¹ His early work has been criticised because the measurements were made over a low temperature range in which impurity conduction may have been an important factor.^{1a} Since the specimen was a thin film rubbed into a quartz surface, the impurity centres may have been dislocations.

With one exception, values for the energy intervals of the phthalocyanines have been obtained by measuring the resistivities of the stable β -crystal form. From a wide range of experimental methods using various specimens, it is concluded that the value for the energy interval of the phthalocyanine β -form lies between 1.5 and 1.7 ev.^{1a} A much lower value, 0.5 ev, is reported for the energy interval of the α -modification of the metal-free phthalocyanine.²² Eley and Parfitt^{17b} report that the conductivity of the α -form is approximately ten times greater than the conductivity of the β -form, whereas Wihksne and Newkirk²² report that the electrical conductivity of the α -form is more nearly 100,000 times greater than that of the β -form at the transition temperature.

The conductivity of phthalocyanine polymers has been investigated in attempts to reduce the values of the energy interval characteristic of the single phthalocyanine unit. In Table 2 are given the values of ϵ , the energy interval, for a few phthalocyanine polymers. Difficulties associated with the purification of the polymers, as well as the lack of practical methods for determining polymer size, have complicated the interpretation of these results. Because of these difficulties, the estimates of the extent of polymer-

²¹ Vartanyan and Karpovich, *Doklady Akad. Nauk. S.S.S.R.*, 1956, **111**, 561.

²² Wihksne and Newkirk, *J. Chem. Phys.*, 1961, **34**, 2184.

TABLE 2. *Energy interval values for polymeric copper phthalocyanine compacts*

Extent of polymerisation	ϵ (eV)	Sample form	Atm.	Ref.
monomer	1.5—1.7	average value	vac.	<i>a</i>
dimer	0.7—1.0	below 7,000 kg./cm. ²		<i>b</i>
five units	0.12—0.26	1,400—14,000 kg./cm. ²	vac.	<i>c</i>
ten units	0.81—0.95	lightly packed cryst.	N ₂	<i>d</i>

^a Eley, *Research*, 1959, **12**, 293; ^b Lawton and McRitchie, "Research on Thermostable Molecules and Polymers," Report No. 57-642, Battelle Memorial Institute, Columbus, Ohio, 1957; ^c Epstein and Wildi, *J. Chem. Phys.*, 1960, **32**, 324; ^d Felmayer and Wolf, *J. Electrochem. Soc.*, 1958, **105**, 141.

isation are, at best, approximations. Lawton and McRitchie⁹ estimated the size of the polymeric unit from probability considerations based on the ratio of the relative amounts of reactants. Felmayer and Wolf¹⁰ used the results of the elemental analyses and theoretical calculations to compute the extent of polymerisation. Using the measured ϵ value and the Eley equation,^{1a,17a} Epstein and Wildi⁸ estimated the polymer to contain five phthalocyanine units having 140 π -electrons.