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Semiconductivity, Optical Properties, and EPR Spectra of Phenothiazine Derivatives in the Solid State

A. ORTIZ, J. I. FERNÁNDEZ-ALONSO, AND A. PARDO

Departmento de Quimica-Física y Química Cuántica, Centro Coordinado CSIC-UAM, Universidad Autonoma de Madrid, Cantoblanco, Madrid, 34, Spain

AND J. LLABRÉS

Departamento de Física Aplicada, Universidad Autónoma de Madrid, Cantoblanco, Madrid, 34, Spain

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The optical, EPR, and electrical properties of phenothiazine derivatives have been investigated as a function of R_2 substituents. Diffuse reflectance spectra show a charge transfer complex transition between 600 and 1100 nm. The EPR spectra show the existence of the radical cation with an unpaired electron per molecule; also there can be seen a dependence of the bandwidth on the R_2 substituents. Measurements of electrical conductivity show a semiconductor behavior in the studied temperature range; the values show as well a dependence of conductivity on R_2. The estimation of the drift mobility of charge carriers seems to indicate a hopping mechanism for the charge conduction.

Introduction

The physicochemical study of phenothiazines has increased greatly during recent years due mainly to its pharmacological applications. This interest has been centered, to date, on the study of dissolved forms with different oxidizing agents (*1*) and, in particular, the monooxidized form, referred to as the cation radical, with the following formula:

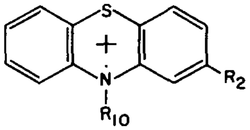

FIG. 1. Cation radical of phenothiazine derivatives.

The cation radicals of the phenothiazine derivatives were first obtained in 1913 by Pummerer and Gassner (*2*). From that time, research concentrated upon the salts of these compounds and in particular on the solutions of these salts (*3*). Only recently the solid phase of these radicals has been studied (*4*).

These cation radicals have interesting properties derived in part from the electronic structure and in part from the form in which the radical is packed in the solid state.

It is assumed that the cation radicals pack together as solids in columns (*4*) in such a way that the partially filled π orbitals of each radical overlap, forming energy bands belonging to the crystalline complex

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TABLE 1

PRODUCT σ (ROOM TEMPERATURE), σ_0 (EXTRAPOLATED), E_a, AND g_1, g_2, g_3

Product	R_2	σ_1 $((\Omega \cdot \mathrm{cm})^{-1})$	σ_0 $((\Omega \cdot \mathrm{cm})^{-1})$	E_a (eV)	g_1	g_2	g_3
Perazine	H	4.6×10^{-9}	5.4×10^{-3}	0.37	2.009	2.007	2.004
Thiethylperazine	$-SCH_2CH_3$	4.4×10^{-7}	3.2×10^{-1}	0.36	2.009	2.007	2.003
Prochlorperazine	–Cl	5.3×10^{-6}	1.3	0.32	2.009	2.007	2.003
Trifluorperazine	$-CF_3$	1.9×10^{-5}	1.4×10^{-3}	0.11	2.009	2.007	2.004

(*5*). The solid phase can be described thus:

$$(Q^+ \ldots Q^+ \ldots Q^+ \ldots Q^+ \ldots)$$

$$(Q^0 \ldots Q^- \ldots Q^{2+} \ldots Q^0 \ldots),$$

where each Q^+ is a cation radical.

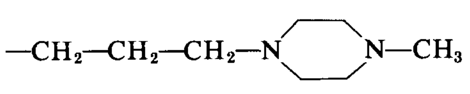
Techniques such as EPR, diffuse reflectance, and electronic conduction applied to the solid state can give useful information on these radicals. The present paper describes the preparation of cation radicals of four phenothiazine derivatives in the solid state. The EPR spectra, diffuse reflectance spectra, and dark conductivity have been measured as functions of temperature. We have tried to relate the results to the packing in the solid state and the influence of the R_2 substituents.

Experimental

(*a*) *Compounds*

The phenothiazine derivatives studied are perazine, thiethylperazine, prochlorperazine, and trifluorperazine; they were supplied by various pharmaceutical laboratories.

The R_{10} substituent is identical for all samples and its formula is the following:



The R_2 substituents are given in Table I. In order to obtain the cation radicals, the Merkle–Dische method (*6*) was used. Extremely brittle crystals were obtained. The melting point of these products ranges between 175 and 223°C.

The stability of these cation radicals in the presence of air is complete and no change is experienced in their composition or properties even after a considerable length of time.

(*b*) *EPR Spectra*

EPR spectra were recorded using a Jeol Jespe-pe spectrometer working in the X band. All recordings were carried out at room temperature. Samples were placed inside a quartz capillary and measured in the presence of air.

(*c*) *DR Spectra*

A Beckman DK-2A with the corresponding attachment was used. Wavelengths range from 400 to 1500 nm. The radiation source was a tungsten lamp, and a lead sulfide detector was used. Pure samples were used as well as samples where the salt under analysis was dissolved in an optically inert KBr or naphthalene matrix. Identical spectra were obtained for both the pure and dissolved samples. The ratio between the cation radical and solvent was 1 : 200.

(*d*) *Dark Conductivity*

Conductivity measurements were carried out under continuous flow using the method described by Masuda (*7*). Potentials of 2 to 20 V were applied.

The thermal variation in the conductivity was measured by placing the sample in a hermetically sealed and opaque cell which was placed inside a thermocontrolled furnace. Temperatures were controlled to ±0.5°C in each measurement. Measurements were taken with a copper–constantan thermocouple, placed beside the sample holder, and a high-precision mercury thermometer inside the cell. Results for both measurements coincided and it could therefore be concluded that the errors in the temperature measurements were less than 1%.

It should be pointed out that because of the impossibility of obtaining sufficiently large monocrystalline samples, we used the classical compressed powder technique and worked throughout under the same experimental conditions. We could thus carry out a comparative analysis of the prepared samples. The conductivity values obtained from randomly oriented grains can be considered as the average conductivity in all directions or as shown in TCNQ (*8*); only the lowest conductivity components determine the value of the variable.

The pellets measured 0.5 cm in diameter and 0.6–0.7 mm in height. Pressing was carried out at 2 tons/cm^2 for 30 min. As any water absorbed between grains would alter the results, this was eliminated first by extracting the air from the press using a standard vacuum pump and second by drying the sample in an oven at 50°C for 24 hr.

At first we tried to carry out a metal–sample contact by evaporating Al at 10^{-6} Torr. This contact showed barrier character. Contact with silver paint on the sample was ohmic, so this silver contact was used on each base of the pellet as well as in the guard ring. The Ag had been dried at 50°C for 2 hr.

Results

1. EPR Results

The spectra for the four products are displayed in Fig. 2. It is observed that they are fairly similar and their trace appears to indicate that the unpaired electron is situated in an axial symmetry field. These spectra, however, are better simulated using an orthorhombic symmetry field. The primary difference in the signals is not in the value for *g*, but in the bandwidth.

The spectra do not present hyperfine structure, and this fact, together with the bandwidth and the *g* values, which were greater than that for the free electron, appears to indicate that the unpaired electron is mainly located on the nitrogen in the four samples.

The variation in these compounds of the R_2 substituents slightly affects the EPR signal and, in particular, its bandwidth. This variation could be attributed to dipole interaction although it is more probably due to the delocalization of the unpaired electron on the nitrogen.

2. Diffuse Reflectance Results

Figure 3 shows the diffuse reflection spectra of the four products. In order to

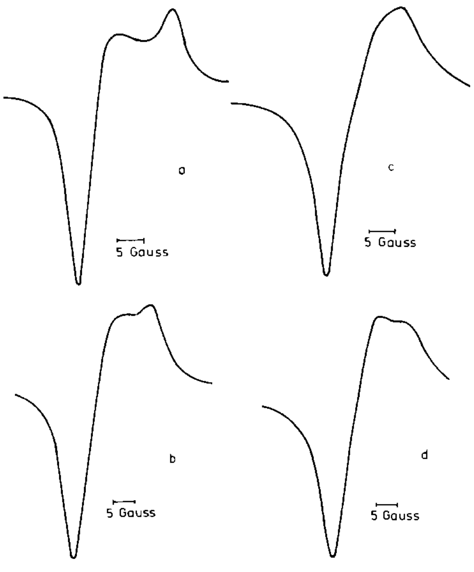


FIG. 2. EPR spectra of: (a) perazine; (b) thiethylperazine; (c) trifluorperazine; (d) prochlorperazine.

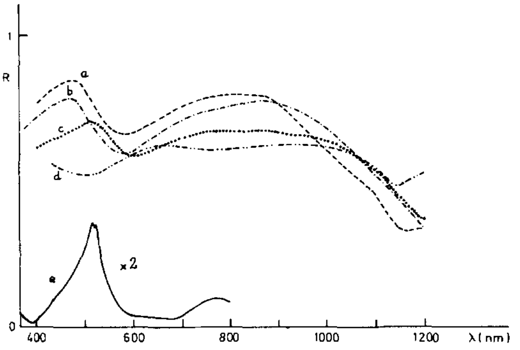


FIG. 3. Diffuse reflection spectra of: (a) trifluorperazine; (b) perazine; (c) prochlorperazine; (d) thietilperazine. (e) Visible spectrum of perazine in sulfuric 9 *N* solution.

study these spectra a comparison was made with the visible spectrum of the cation radical of perazine in solution.

The diffuse reflection spectra contain two bands, one at 500 nm and a very wide one of equal intensity at a much greater wavelength (from 600 to 1200 nm). From 1200 to 2000 nm, there is no other transition.

The position of the first band corresponds with the spectrum of the same radical in solution, 515 nm, although it is slightly displaced toward the blue zone. These transitions of the monomer are affected by the field of the other cations which causes a shift in the π–π^* bands. The second band is wide and of intensity equal to that of the former. This band exhibits typical characteristics of a charge transfer: wide, without defined maxima.

These TC bands appear to superpose upon the vibrational structure of the radical cation in solution (see Fig. 3, curve e) which is observed at 750–870 nm. It can be explained if we consider that the TC band in the solid is more intense than the vibrational transitions.

The TC band in the diffuse reflection spectra for the perazine family varies slightly from 900 nm. A quantitative difference between the TC of these radicals is not observed. It could be deduced that the R_2 substituents do not exert much influence upon the TC.

A TC is produced in the solid state because these cation radicals are sufficiently close to overlap their half-complete π orbitals. A possible structure of these ions could be in the form of infinitely long chains or columns (*9*). This type of structure has been proposed for several ion salts. The columns are believed to be formed by equidistant ion radicals (*10*). The structure in columns and the interplanar distance between the ions comprising the column can form charge transfer complexes. With two identical radicals, greatest interaction would take place when two ions are superposed. But a fact that appears to have a marked influence on the packing distance of the cation derivatives is the existence of the R_{10} substituents, which are capable of producing a large steric effect when interposed between two radicals of the same column. This steric effect seems to be of larger intensity than the effect produced by the influence of the R_2 substituents, so the R_2 effects seem to be nullified.

3. *Dark Conductivity*

Figure 4 shows σ versus $1/T$. It is observed that the cation radicals obey the equation

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

where σ_0 is the conductivity for $T \rightarrow \infty$, E_a is the activation energy of the electrical conduction, and k is the Boltzmann constant. The results show that the electrode–sample contacts behave ohmically. Table I gives values for σ_0, σ_1 (at room temperature) and E_a for each of the compounds under study. The values of σ measured at room temperature vary from 10^{-9} to 10^{-5} $(\Omega \cdot \mathrm{cm})^{-1}$, indicating that the compounds studied exhibit an intermediate-type conductivity (*11*).

The activation energies varied between 0.37 and 0.11 eV.

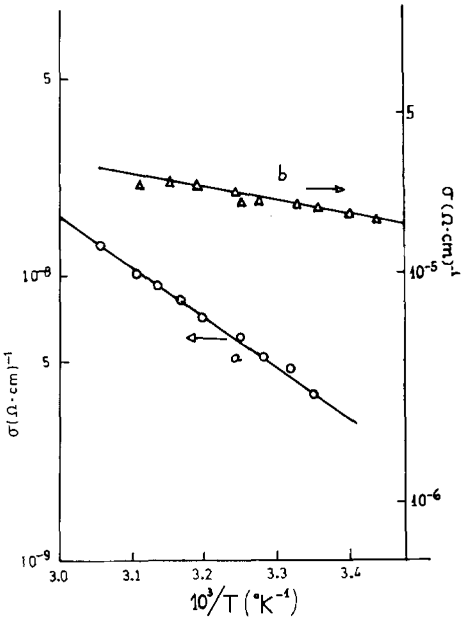


FIG. 4. Log σ versus $10^3/T$: (a) perazine (b) trifluorperazine.

We attempted to prove the existence of an optical transition for the wavelengths corresponding to the associated energies of the electronic activation processes. The attempt, however, proved negative.

The prochlorperazine showed anomalous behavior, similar to that of the neutral chlorpromazine as previously described by Gutmann and Netschay (*12*).

An interesting characteristic regarding the charge transfer in the solid state is the evaluation of the mobility of the carriers. The Hall effect is the usual technique for studying inorganic semiconductors; organic semiconductors exhibit very low values for electronic mobilities and the technique cannot, therefore, be used. The carrier density was then determined from the plasma frequency. This equals 1200 nm and corresponds to a density of $n = 10^{20}\ e/cm^3$.

This value shows that each molecule contributes an electron to a hypothetical conduction band. Therefore, using this value for n and the expression

$$\sigma_0 = en\mu,$$

where e is the elemental charge, the electron mobility, μ, can be calculated. Values obtained were within the range 10^{-4} to 10^{-2} cm/V · sec and are typical for aromatic compounds when measurements are made on pressed powder. This suggests, in agreement with Many and Harnik (*13*), that the conduction mechanism can be of the "quantum hopping" type.

Conclusions

The most important difference between organic and inorganic semiconductors arises from the fact that the molecules in the crystalline state are held together by small forces and are fixed at relatively long distances from each other (around 3.4 Å). In many organic solids this restricts the intermolecular transport of charges. Dark conductivity as well as photoconductivity properties are related to the electronic and structural behavior of pure organic compounds, and also to those in the polycrystalline state (*14*).

In our case each compound is made up of a tricyclic nucleus, a relatively long R_{10} lateral chain, and an R_2 substituent, as well as the ClO_4^- ion, which is common to the four derivatives studied. It can be assumed, through the EPR, that the presence of a radical with a free electron is identified.

The influence of the R_2 substituents can be associated principally with the bandwidth either by changing the position of the electron on the nitrogen or by increasing the dipole interactions of the radicals, though probably these dipole interactions could be considered as a result of alterations of the electron on the nitrogen by the R_2 substituents.

It can be appreciated that the product with highest conductivity is that displaying the narrowest bandwidth (see the EPR spectrum for trifluorperazine).

From the diffuse reflectance, it is observed that a charge transfer takes place as a result of the presence of a free electron in each radical. However, it is known that steric effects result from the intermolecular geometry and the nature of the substituents plays an important role in intermolecular charge transfer because of the packing of adjacent radicals in the solid state (*15*). This leads us to believe that the effect of the lateral R_{10} chain is considerably greater, for steric reasons, than the effect caused by the R_2 substituents. We are further investigating this fact by carrying out various diffraction studies using X rays.

Dark conductivity is related to the electronic and structural behavior of pure organic compounds and is closely connected with the number and degree of aromatic rings or R substitution effects on the conductivity. This is enhanced by increasing the electron donating power of the group R (*16*).

The increase in σ of these compounds (see Table I) is probably due to the effect of the R_2 substitution on the π eletron system of the phenothiazine nucleus. In the case of trifluorperazine we have to consider the electrophilic nature of the R_2 which gives rise to an electronic defect in the phenothiazine nucleus. This should diminish the conductivity but instead it is found experimentally that it is increased, probably because there is formed a dipole species of the cation radical (*16*), which should favor conductivity.

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