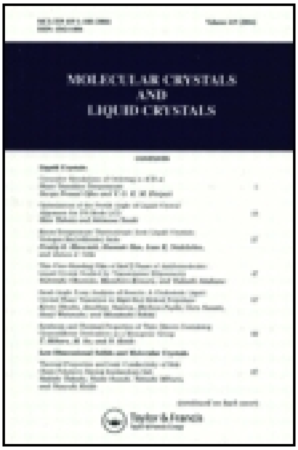

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A. Ortiz [a] , A. Pardo [a] , M. Poyato [a] & J. I. Fernandez-alonso [a]

[a] Departmento de Quimica-Fisicay Quimica Cuántica, Centro Coordinatdor CSIC-UAM, Facuited de Ciencias C-XIV, Cantoblanco (Madrid, 34), Spain

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Influence of Substituents in the Solid State of Radical Cations of Two Phenothiazine Derivatives

A. ORTIZ, A. PARDO, J. M. POYATO and J. I. FERNÁNDEZ-ALONSO

Departamento de Quimica-Fisica y Quimica Cuántica, Centro Coordinador CSIC-UAM, Facultad de Ciencias C-XIV, Cantoblanco (Madrid, 34), Spain

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The optical, EPR and magnetic susceptibility of the cation radicals of two phenothiazine derivatives have been investigated as a function of R_2 and R_{10} substituents. We have tried to relate all of the above with the conductivity of these compounds and their slight dependence of the conductivity on the temperature. The diffuse reflectance spectra show a charge transfer between 600 and 1200 nm. This CT band shows the R_2 and R_{10} substituents influence. The EPR shows the existence of the radical cation and the dependence of the bandwidth on the R_{10} substituents. X static measurements give different quantities of free unpaired electrons on each radical in the solid state, also related to the R_{10} substituents.

INTRODUCTION

The significance of the semiconductivity of organic dyes and other classes of organic solids, such as charge-transfer complexes, which behave in some ways like metals[1] or polymers[2] is today beyond doubt. It is now known that the dark- and photoconductivity are connected with the structure of the organic conductors.[3] The most important difference between organic and inorganic semiconductors arises from the fact that the molecules in the crystalline state are held together by weak forces and are located at relatively long distances from each other (of the order of 3,4 A).

We report here on the preparation and solid state properties of two cation radical salts. There are two reasons for focusing on the solid state properties of phenothiazine radicals; first, there is the possibility of obtaining new interesting solids or of permitting systematic studies—as there has not been reported a systematic study on solid state properties; and, second, the specific interest is their close similarity to the organic conductor NMP-TCNQ,[4,5] where the NMP^+

is the diamagnetic 14 electron cation of *N*-methylphenazine.[6] Besides, the preparation of the cation radical salts of the two phenothiazine derivatives provides us of a simpler case of study CT complexes, than the NMP-TCNQ complexes with two types of stacks, where the contribution of each stack is more difficult to ascertain.

Studies of EPR and electrical conductivity, which have been among the most fruitful of pursuits, together with the electronic spectra and the Xm susceptibility, which have been traditionally applied for elucidating the electronic structure of molecules and solids, should be able to produce some information concerning the interaction in the solid state of the ion radicals.

It is assumed that the phenothiazine derivatives cation radicals in the solid state can exist in different arrangements, thus:

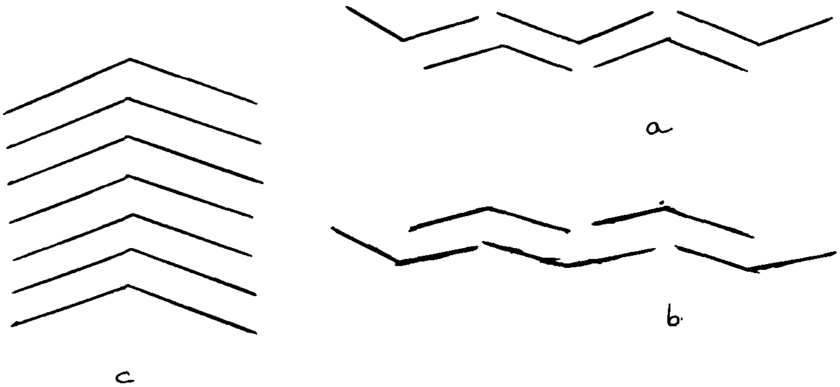

FIGURE 1 Possible arrangements of the phenothiazine derivative cation radicals in the solid state.

where each folded figure (*) stands for a phenothiazine derivative cation radical viewed along the direction connecting the nitrogen and sulfur atoms. The partially filled π orbital of each radical will overlap with the nearest radical. This overlap could be primarily of two types: either the interaction is between a pair of adjacent radicals, that is a dimer type interaction, or, if the interaction is strong enough, it would be by more than pairwise.[7] However, the introduction of bulky substituents, such as the R_{10} lateral chain or even the R_2 substituents, contributes to the change of the more than pairwise interaction of ion radicals into the pair-by-pair interaction.[8]

The present paper describes the preparation of the cation radicals of two phenothiazine derivatives in the solid state, the EPR spectra, diffuse reflec-

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* The studies carried out at the CSIC using EPR technique showed that these radicals in solution have the same angular structure of the neutral phenothiazine.

tance spectra, and magnetic susceptibility related to dark conductivity as a function of temperature. We have tried to relate the results with the influence of both R_2 and R_{10} substituents in the solid state.

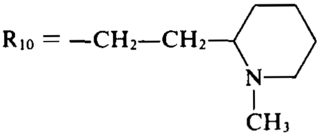
EXPERIMENTAL

a) Compounds

The phenothiazine derivatives studied are Thioridazine and Metoxipromazine, supplied by various pharmaceutical laboratories.

I R_2—OCH_3 R_{10} = —CH_2—CH_2—CH_2—$N(CH_3)_2$

II R_2—SCH_3



The general formula is shown in Figure 2.

In order to obtain the cation radicals, the Merkle method[9] was used; no single crystals were obtained by this method. The melting points of these products are: 226°C-Thioridazine and 224°C-Metoxipromazine.

The elemental analysis of these compounds gave: for Thioridazine-C: 43,86%; H: 4,85%; N: 4,79%; S: 6,04%; Cl: 12,64%. Metoxipromazine-C: 41,53%; H: 4,71%; N: 5,40%; S: 6,04%; Cl: 12,60%. This stands for: (PHT derivative) $^+ClO_4^-ClO_4H \cdot H_2O$. The UV and visible spectra of these products in solution were given in a previous work.[10]

Both products are dark blue; the stability of these radicals in the presence of air is total and no change is observed in their composition or properties even after a considerable length of time.

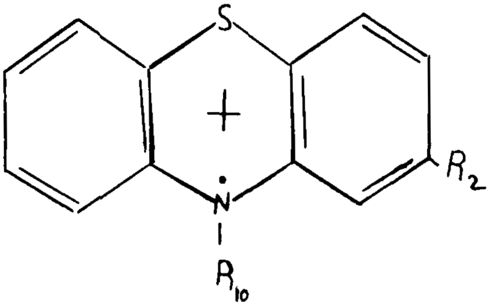


FIGURE 2 Molecular structure of phenothiazine.

b) EPR spectra

EPR spectra were recorded using a JEOL, Jespe-pe spectrometer working in X band. All recordings were carried out at room temperature. Samples were placed inside a quartz capillary and measured in the presence of air. The microwave power was 10 mW, enough to not saturate the resonance, and the field modulation was 0,4 gauss; both spectra are derivative spectra. The accuracy is ±0.001, the standard taken is DPPH.

c) D.R. spectra

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

d) X measurements

The paramagnetic susceptibility was determined by the Faraday method. The samples in powder form were tightly packed in quartz tubes 4 mm ϕ and 8 mm height, the tubes were suspended between the constant gradient pole pieces of a B-M6 Bruker electromagnet by a thin quartz fiber from the beam of a 4411 Sartorius electro-balance, the force acting on each sample weighing approximately 0,06–0,07 gr is of the order 10^2 μg depending on the magnetic field H at a 3 cm gap between polar pieces $H \cdot dH/dX = 21{,}54$ Kgaus^2/cm for 30 amp. and $H \cdot dH/dX = 12{,}21$ Kgaus^2/cm for 20 amp; for the elimination of ferromagnetic impurities X was obtained from a (X, 1/H) plot by extrapolation of $H - \infty$. Slopes of the order of 10^{-3} to 10^{-4} gauss were obtained; i.e. the samples contained relatively low concentration of ferromagnetic impurities with reference to the standard sample used, which was $C_{10}H_{22}$ (Merck). For this, a value of $X = 0{,}8423.10^{-6}$ cgs was taken.[11]

Each sample was measured ten times at two different field strengths (13,35 and 10,33 Kgaus) in a vacuum of 10^{-2} torr. The accuracy of the measurements of X is believed to be ±1%.

EPR SPECTRA

The spectra of the two cation radicals are displayed in Figure 3. Product II (thioridazine) shows very clearly an asymmetrical pattern, consisting of three peaks due to the g-factor anisotropy; its values are $g_1 = 2.009$, $g_2 = 2.007$ and $g_3 = 2.003$, and though its trace seems to indicate that the unpaired electron is situated in an axial symmetry field, the spectrum is better simulated using an

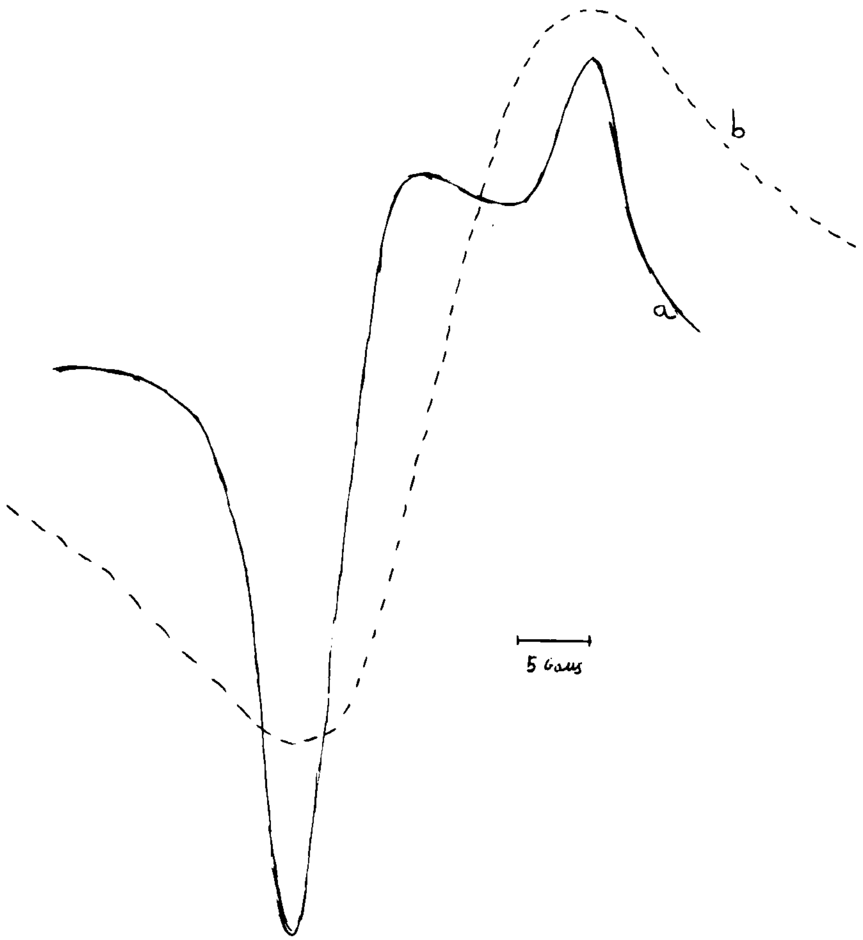


FIGURE 3 EPR spectra of: a) Thioridazine, b) Metopromazine.

orthorombic symmetry field. For product I (metopromazine) the spectrum shows only one line with a g-value of 2.006.

As the system is an undiluted paramagnetic, the spectra do not present hyperfine structure and this fact, together with the large linewidth and the g values, greater than that for the free electron, impedes the localitation of this electron, though it seems to be located on the nitrogen of the phenothiazine nucleus in the same products in solution.

The variation of the R_2 and R_{10} substituents in these compounds affects the EPR signal mainly in its band width; this variation could be attributed basically to steric effect produced by the voluminous R_{10} of compound II (thioridazine) which will diminish the interaction between the radicals in the solid state.

SOLID STATE SPECTRA

The effects of intermolecular interaction are more significant in radical salt crystals than in any other type of molecular crystals, since the unpaired electron on each radical will make a bonding between one or more radicals. The covalent force binds the radicals close to each other, while the exchange repulsion of the closed-shell electrons, including the so-called steric repulsions, increase the radical–radical distances. The positive charge on each ion is also repulsive in the present system. The analysis of these intermolecular forces might be difficult; however, the actual packing structure represents a balance of these several opposite forces.

In order to characterize the solid state spectra of these cation radical salts, it will be necessary to compare them with the absorption spectra of the same radicals in solution.

First, we have the spectra of the metoxipromazine in the solid state (Figure 4a). This spectrum contains two bands: one at 500 nm and another very wide one of equal or higher intensity at a much longer wavelength from 600–1200 nm. There is no other transition in the rest of the field until 2000 nm. The position of the first band matches the spectrum of the same radical in solution 573 nm (Figure 4b), although it is slightly displaced towards the blue. These transitions of the monomer are supposed to be affected by the field of the other cations and cause a shift in the $\pi \rightarrow \pi^*$ bands.[12]

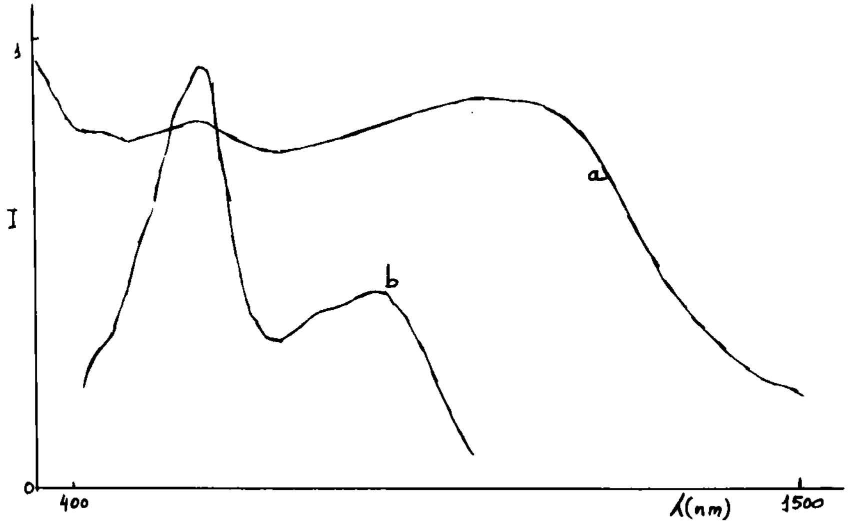


FIGURE 4 a) Solid state, diffuse reflection spectrum of Metopromazine, b) Visible spectrum of Metopromazine in sulphuric 9N solution.

The second band is wide and more intense than the former and exhibits the typical characteristics of a charge transfer: wide and without well defined maxima. This transfer band appears to have a maximum at about 1200 nm while at 800 nm there is a slight shoulder which could be attributed to the electronic vibrational structure of the monomer in solution, that appears at 760–860 nm.

In the thioridazine spectrum (Figure 5a), three maxima can be observed. The first corresponds with the 650 max. of the spectrum of the same radical in solution (see Figure 5b); there is no absorption at 490 nm in the solid state, and the max. at 900 nm due to vibrational structure, seems to be displaced towards the blue in the solid state spectrum. Only the absorption from 900–1500 nm can be considered as a CT band produced by the interaction between the umpaired electron of the half filled π orbital on each radical.

This band appears regardless of the charges in the radicals; therefore interaction between the unpaired electron must be essential for the appearance of the new absorption band. The interaction of the single occupied orbital of a radical with the nearest radical is greatly dependent on the relative interatomic distance and orientation and a small change in these factors may cause a somewhat large change in the overlap integral: this change produces the different intensity of the charge transfer absorption.

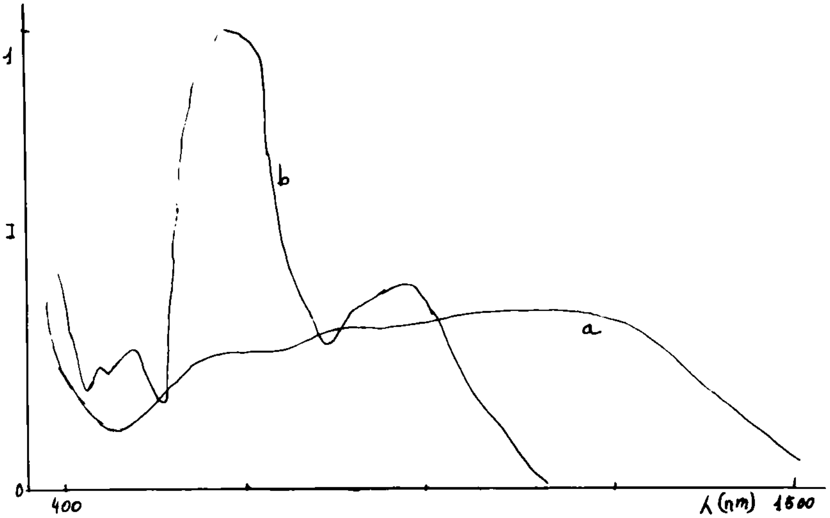


FIGURE 5 a) Solid state, diffuse reflection spectrum of Thioridazine, b) Visible spectrum of thioridazine in sulphuric 9N solution.

On the contrary, the excitation energy of the transition is not greatly influenced by a small change in the intermolecular distance of mutual orientation between the ionization potential and the electron affinity of the phenothiazine monopositive cation radical. This is in agreement with the observed slight sensitivity of the band positions in the cation radicals.

However, there still remains to be ascertained whether these bands are due to a CT between only two radicals forming dimers, since part of their location span is the same as that of the phenothiazine bromide in solution[12] or whether they are also due to more than a pairwise interaction, for the absorption bands extend over a long range and this seems to be intimately connected with the large electron overlap between the radicals.[13]

MAGNETIC SUSCEPTIBILITY

It is known that the charge transfer interactions between the ion radicals will be reflected through a marked decrease in paramagnetic susceptibilities of these salts.[12,8] The charge transfer interaction is known to stabilize the antiferromagnetic state where the spins associated with the ion radicals are antiparallel.

This seems to be the case with the present cations:

Mol Wt.	Observed Susceptibility at 294 K (cgs/mol)	Assumed Diamagnetic (cgs/mol)	Paramagnetic Susceptibility (cgs/mol)	Radical Concentration, %
I-532,38	$+15{,}59\cdot 10^{-6}$	$-273{,}9\cdot 10^{-6}$	$+289{,}5\cdot 10^{-6}$	47
II-588,52	$+236{,}5\cdot 10^{-6}$	$-320{,}\cdot 10^{-6}$	$+556{,}6\cdot 10^{-6}$	64

The diamagnetic contribution was estimated from the value of the diamagnetic susceptibilities of components, on the assumption that the value for a neutral organic molecule may be used in place of the value for the molecular ion (though when the neutral organic molecule is changed to ion, it may become coplanar and this would result in a small increase in diamagnetic susceptibility) the values for Metopromazine and Thioridazine as well as the H_2O molecule were taken from Pascal's constants and for ClO_4^- from L. N. Mulay.[14]

Therefore, these products are paramagnetic with 47% and 64% free unpaired electrons and the difference of the paramagnetic values must be necessarily related to the interaction degree of the radicals in the solid state which could be attributed to the steric effects of the R_{10} substituents upon these interactions.

Although it is not clear, at present, whether the spin exchange interaction can be described by the singlet-triplet model or by the linear chain Heisenberg model, it can be seen that the charge transfer interaction between the cation radical makes a significant contribution to the antiferromagnetic spin exchange interaction. A qualitative explanation can be made considering (following Hausser and Murrell[15]) a particular pair of adjacent radicals in a chain. The interaction of this pair gives rise to a singlet (non-magnetic) state and a triplet (magnetic) state, for which the relative position is determined, to a first approximation, by an exchange integral between the paired radicals.

If the singlet-triplet excitation energy, to which the spin exchange in the charge-transfer contributes, is small, the triplet state may become thermally accessible and paramagnetism can be observed. Therefore, the charge transfer configurational interactions also contribute to the determination of the relative energy levels of the magnetic and non-magnetic states. Consequently, it appears that the spin exchange coupling parameter will depend on the relative energy of the exchange interaction and on the charge transfer configurational interaction effects.[16]

RELATIONS WITH THE SUBSTITUENTS R_2 AND R_{10}

In a previous work[17] the conductivity of a series of radical cations of phenothiazine derivatives was presented: these salts show a wide range in their conductivity; such variation is not surprising considering the variety of possible crystal structures within this family and this allows a certain, though necessarily crude, correlation of conductivity with structure. The first similarity in these two cation radicals is the very slight dependence of σ with temperature along the range studied, from room temperature to 80°C, the conductivity of these compounds is:

	σ room $(\Omega\ \mathrm{cm})^{-1}$	σ_0 $(\Omega\ \mathrm{cm})^{-1}$	Ea (eV)
Metopromazine	$1{,}36 \cdot 10^{-4}$	$5{,}5 \cdot 10^{-2}$	0,18
Thioridazine	$1{,}45 \cdot 10^{-7}$	$2{,}5 \cdot 10^{-4}$	0,19

There are references of several organic semiconductors with analogous behavior;[18,19] however, in our case, the lack of an open shell, organic type, acceptor, will reduce the problem to the packing of the cation radicals in the solid state. Two effects must be considered:

a) Compared with other derivatives with R_2 = —H, the —SCH—SCH_3 and —OCH—OCH_3 substituents are capable of producing a structure where conductivity is nearly temperature independent—and that is so because these substituents are capable of modifying the chemical structural characteristics of these phenothiazine derivatives through charge distribution, orientation and strength of dipoles, polarizibility and the ability to form hydrogen bonds and so are capable of determining the molecular packing, and therefore, the conductivity behavior. In addition, both substituents have a similar strong electron donating power upon the π electron system of the phenothiazine nucleus. So these substituents will tend to compensate the radical electronic defect and consequently the repulsions between the radicals in the solid state will diminish, thereby facilitating conductivity.[20]

b) R_{10} substituents effect. It is known that the steric effect results from the internal molecular 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.[21] Thus, it can be seen that the differences in conductivity of these two compounds could be related to the length of the R_{10} chain and to the steric effect due to the chain being located between two neighboring radicals. The lateral chain of product II is more bulky than the R_{10} chain of I; therefore, the steric effect of II is stronger by the interposition of the chain between two adjacent cation radicals, which impedes the current flow; this fact can explain the difference in conductivity values between the two cation radicals.

The effect of these substituents appears on the other properties studied. The EPR spectra show that in I there is only one line, wider than that of II spectrum. This indicates clearly that I is a better conductor as a consequence of the minor steric effect of R_{10} substituent in product I with respect to the steric effect produced by the R_{10} in product II.

The D.R. shows that the electron donating power of the R_2 substituents dominates the R_{10} steric effect. It could be thought that the R_2 produces a slight displacement of the CT band and the R_{10} a variation of its intensity.

With the magnetic susceptibility it can be seen that the metopromazine has 47% and Thioridazine 64% of free unpaired electrons. This must be also a consequence of the steric effect of the R_{10} substituents of the latter product. Its more bulky chain will increase the separation between two radicals and so the interactions among the radicals will diminish; therefore, the conductivity will be lower in II than in I.

Consequently, it could be thought that in the solid state each substituent will characterize a defined structure or packing while the R_{10} substituents will produce a variable steric effect upon the structure. This, however, will have to be proved by X ray structure studies.

Thus, this type of compounds shows interesting characteristics to be studied as semiconductors, such as longtime thermal, chemical and electrical stability; they can also be vacuum sublimed or evaporated, without decomposition, obtaining thin fils for photoconductivity, besides, the extremely broad absorption spectra, ranging from visible to near IR wavelengths, enhance their applications as such. However, conductivity is clearly diminished by the steric effects of the R_{10} substituents. It could be deduced that products without such substituents would enhance their possibility as semiconductors.

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