CHARGE-TRANSFER COMPLEXES OF PHENOTHIAZINE DERIVATIVES WITH π-ELECTRON ACCEPTORS

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UDC 547.869.2:541.49

Charge-transfer complexes (CTC) of some phenothiazine derivatives with π-electron acceptors were obtained. They were used to determine the ionization potentials of the investigated donor compounds. The complexing constants of phenothiazine and some of its N-substituted derivatives were found. The experimental data obtained make it possible to draw conclusions relative to their configurations.

The investigation of the effect of complexing on the optical and magnetic properties of organic compounds elicits great interest in view of the possibility of the use of the molecular complexes as organic semiconductors, catalysts in organic synthesis, biocatalysts, etc.

Phenothiazine and its derivatives have clearly expressed electron-donor character and biological action [1-3]. The semiconductor properties of a phenothiazine–iodine complex were detected in [1] and the development of a cation radical during complexing was established. The ionization potentials of a number of phenothiazine derivatives were determined by means of the charge-transfer complexes (CTC) [2, 3], and the problem of the geometry of the CTC of phenothiazine with sym-trinitrobenzene was examined by x-ray diffraction analysis [4].

We have previously shown [5, 6] that the electronic absorption spectra of a number of phenothiazines, the electronic density, and the bond order depend both on the character of the substituents and on the three-dimensional structure of the phenothiazine molecule; i.e., substitution at the nitrogen atom of the hetero-ring leads to an intra- or extraconfiguration of the compound. This shows that the electron-donor character, which is associated with the ionization potential, of various phenothiazine derivatives will depend on both the character and orientation of the substituents and on the three-dimensional structure [7].

It is known that when a CTC is formed, one can observe one or several bands in the absorption spectrum that are not affiliated with either the donor or the acceptor. This band (or bands) is associated with charge transfer from the donor to the acceptor. In conformity with [8], the charge-transfer transition energy ($\Delta E = h\nu_{CT}$) depends on the electron affinity of the acceptor (E_A), the ionization potential of the donor (I_D), and the dissociation energy of the excited state (W):

$$h\nu_{CT} = I_p - E_A - W \quad (1)$$

If we consider a number of complexes of the same acceptor with different electron donors, we can, proceeding from [8], to a good approximation write

$$h\nu_{CT} = I_p + \text{const} \quad (2)$$

This linear dependence between $h\nu_{CT}$ and I_D of the donor is observed for various CTC [3, 9, 10] and makes it possible to determine unknown ionization potentials of various donors by means of an experimental determination of the charge-transfer energies ($h\nu_{CT}$).

In the present communication, we present data relative to the ionization potentials of some phenothiazine derivatives, which were determined in accordance with Eq. (1) by means of the CTC of a number

Sofia University, Bulgaria. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 497-501, April, 1973. Original article submitted April 24, 1972.

TABLE 1. Charge-Transfer Transition Energies and Ionization Potentials

Chloranil acceptor			Tetracyanoethylene acceptor		
Compound	$h\nu_{CT}$, eV	I_p^{exp}, eV	Compound	$h\nu_{CT}$, eV	I_p^{exp}, eV
Anthracene	1,981[10]	7,55[15]	Naphthalene	2,206*	8,12[17]
Butylamine	2,271*	8,71[13]	Phenol	2,525*	8,52[11]
Diethylamine	2,067*	8,01[13]	Furan	2,755[19]	8,89[13]
Benzylamine	2,206*	8,56[13]	Phenanthrene	2,317[19]	8,03[15]
N,N-Dimethylaniline	1,86[10]	7,20[14]	Aniline	2,032[18]	7,70[13]
α-Naphthylamine	1,905[10]	7,30[12]	N-Methylaniline	1,928[18]	7,38[13]
			N,N-Dimethylaniline	1,761[18]	7,20[14]

*Our data.

TABLE 2. Absorption Bands and Charge-Transfer Transition Energies of the Investigated CTC

Compound	Chloranil acceptor			Tetracyanoethylene acceptor		
	λ_{CT}, nm	$h\nu_{CT}$, eV	I_{CT}, eV	λ_{CT}, nm	$h\nu_{CT}$, eV	I_{CT}, eV
Phenothiazine	725	1,71	6,57	887	1,40	6,58
N-Methylphenothiazine	686	1,81	6,96	880	1,41	6,60
N-Ethylphenothiazine	670	1,85	7,10	870	1,43	6,64
N-Propynylphenothiazine	675	1,84	7,07	838	1,48	6,72
N-Acetylphenothiazine	662	1,88	7,23	680	1,80	7,35
N-Acetyl-3,7-dibromophenothiazine	656	1,89	7,27	654	1,90	7,44
N-Methyl-3,7-dibromophenothiazine	680	1,82	7,00	695	1,79	7,25
3,7-Dibromophenothiazine	710	1,75	6,72	815	1,52	6,79
3,7-Dichlorophenothiazine	715	1,74	6,68	810	1,53	6,81
Diphenylamine	652	1,90	7,31	758	1,64	7,00

TABLE 3. Absorption Bands and Charge-Transfer Transition Energies of CTC of Aniline and Phenothiazine Derivatives with Chloranil

Compound	λ_{CT}, nm	I_p^{exp}, eV	Compound	λ_{CT}, nm	I_p^{exp}, eV
Aniline	530[9]	7,70[13]	Phenothiazine	725	6,57
N-Methylaniline	590[9]	7,38[13]	N-Methylphenothiazine	686	6,96
N,N-Dimethylaniline	675[9]	7,20[14]	N-Ethylphenothiazine	670	7,10

of phenothiazine derivatives with chloranil and tetracyanoethylene in chloroform.

Since one should expect that the three-dimensional structure of the donors will affect the three-dimensional structure of the CTC as well as the rate of its formation, we measured the rate constants for the formation of the CTC of picric acid as the acceptor at 20° in chloroform. Using linear dependence (2), we derived equations that link $h\nu_{CT}$ and I_p for chloranil and tetracyanoethylene. In deriving this dependence we used as electron donors the compounds indicated in Table 1, in which the experimental I_p values taken from [11-15] and the $h\nu_{CT}$ values are also presented. By treatment of these data by the method of least squares we obtained the following equations, which link I_p and $h\nu_{CT}$:

$$\text{For chloranil: } I_p = 3.906\ h\nu_{CT}\ (\text{eV}) - 0.112 \pm 0.1; \quad (3)$$

$$\text{For tetracyanoethylene: } I_p = 1.704\ h\nu_{CT}\ (\text{eV}) + 4.20 \pm 0.1. \quad (4)$$

The experimental λ_{CT} and $h\nu_{CT}$ values of the investigated CTC and the calculated [from Eqs. (3) and (4)] ionization potentials of the investigated phenothiazine derivatives are given in Table 2. It is seen from Table 2 that the introduction of halogen into the benzene rings in the p position relative to the imino group of phenothiazine leads to a small increase in the ionization potential because of the weak electron-acceptor effect of halogens. Replacement of the hydrogen atom attached to the nitrogen by an acyl group leads to the greatest increase in I_p, while substitution by an alkyl group leads to an increase in the charge-transfer transition energy and hence to an increase in I_p.

In a discussion of the spatial orientation of the alkyl group attached to the nitrogen atom [16], it was established that there is a possibility of the development of two configurations (intra and extra) that differ with respect to the spatial orientation of the unshared electron pair of the nitrogen atom.

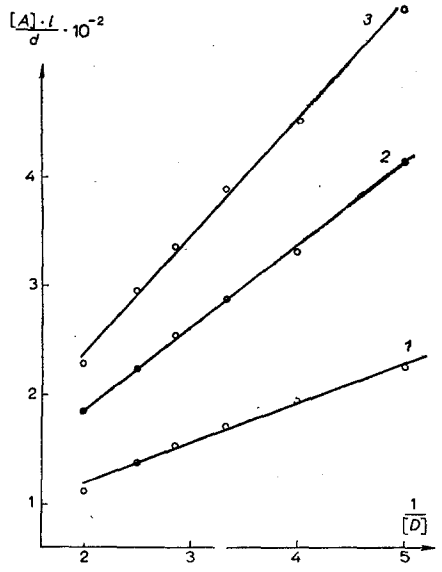

Fig. 1. Dependence of $[A] \cdot l/d$ on $1/[D]$ for complexing of picric acid with phenothiazine (1), N-methylphenothiazine (2), and N-ethylphenothiazine (3).

When the hydrogen atom attached to the nitrogen is replaced by an alkyl group, a hypsochromic shift of the long-wave band by 10-15 nm is observed in the electronic absorption spectra [5]. In addition, a shift in the signal of the α'-protons in the aromatic rings by 0.3-0.4 ppm to weaker field as compared with the α-protons of unsubstituted phenothiazine was observed in an investigation of the PMR spectra of these derivatives [6]. These facts can be explained by a decrease in the participation of the unshared pair of electrons of the nitrogen atom to the overall π-electron conjugation due to a change in the configuration under the influence of bulky alkyl substituents. This transition from the intra to extra configuration leads to weakening of the electron-donor properties of N-substituted phenothiazines and to a decrease in the energy of the upper bonding MO [16]. Hence one should expect a hypsochromic shift of the charge-transfer band. In fact, it is seen from Table 2 that the N-substituted derivatives have a higher ionization potential than phenothiazine. If configuration changes do not occur, replacement of the hydrogen atom by an alkyl group should lead to a decrease in the ionization potentials as a result of the $+I$ effect of the substitutent, as occurs for aniline and its N-substituted derivatives (Table 3). The data obtained from the spectra of the CTC with tetracyanoethylene display the same regularities as in the case of chloranil. Here, however, the charge-transfer band of N-alkyl derivatives of phenothiazine is expressed more weakly.

The spatial orientation of the alkyl radicals in phenothiazine derivatives has a substantial effect on the geometry of the CTC and hinders the interaction between the donor and the acceptor.

We determined the constants of complexing of phenothiazine and N-methyl- and N-ethylphenothiazine with picric acid in chloroform by the method in [17]:

$$\frac{[A]\cdot l}{d} = \frac{1}{\varepsilon_{compl}} + \frac{1}{K_c \cdot \varepsilon_{compl}} \cdot \frac{1}{[D]},$$

where [D] is the donor concentration in gram · moles per liter, [A] is the acceptor concentration is gram · moles per liter, d is the absorption of the complex at a selected wavelength, l is the cuvette thickness in centimeters, K_c is the complexing constant in liters per mole, and ε_{compl} is the molar extinction coefficient of the charge-transfer band of the complex.

The dependence of $[A] \cdot l/d$ on $1/[D]$ is shown in Fig. 1, from which the K_c and ε_{compl} values (Table 4), respectively, were obtained. It is seen that when the hydrogen atom attached to the nitrogen is replaced by an alkyl group the complexing constant (K_c) decreases. This is in agreement with the above conclusions regarding the change in the spatial orientation of the unshared pair of electrons attached to the nitrogen atom in N-substituted phenothiazines.

Using the Hückel method (LCAO MO), we determined the energies of the upper occupied MO (E_m) for some of the donors used in this study. Parameters taken from [6, 16], which correspond to the appropriate configurations, were used in the calculations. It is apparent (Table 5) that there is agreement

TABLE 4. ε_{compl} and K_c Values for Complexing of Phenothiazine Derivatives with Picric Acid

Compound	ε_{compl}	K_c, liter · mole^{-1}
Phenothiazine	380	1,17
N-Methylphenothiazine	280	0,47
N-Ethylphenothiazine	256	0,38

TABLE 5. Energies of the Upper Occupied MO and Charge-Transfer Energies

Compound	Configuration	E_m, β units	$h\nu_{CT}$, eV	I_p, eV
Phenothiazine	*intra*	0,485	1,71	6,57
3,7-Dibromophenothiazine	*intra*	0,507	1,75	6,72
3,7-Dichlorophenothiazine	*intra*	0,499	1,74	6,68
N-Methylphenothiazine	*extra*	0,686	1,81	6,96
N-Methyl-3,7-dibromophenothiazine	*extra*	0,694	1,82	7,00

between the experimental $h\nu_{CT}$ values and the theoretical E_m values; this is also in agreement with the configuration change when the hydrogen of the imino group is replaced by an alkyl group.

EXPERIMENTAL

Concentrations of the order of 10^{-2} M for the donors and 10^{-3} M for the acceptors in chloroform were used to obtain the CTC with chloranil. The picric acid concentration in the determination of the complexing constants of phenothiazine and its N-methyl and N-ethyl derivatives was $1.98 \cdot 10^{-2}$ M. The molar concentration of the donor in all cases was the same – from $2 \cdot 10^{-1}$ to $5 \cdot 10^{-1}$ M. In view of the facile oxidation of phenothiazine and its derivatives, the solutions of the donors were prepared in vessels covered with lightproof paper, and the electronic absorption spectra were recorded immediately after preparation of the solutions. The absorption spectra at 400-750 nm were recorded with an SF-10 spectrophotometer, while the spectra above 750 nm were recorded with an SFD-2 spectrophotometer.

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