CHARGE-TRANSFER COMPLEXES BASED ON INDOLE COMPOUNDS (REVIEW)

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The literature data on the donor–acceptor interaction of indoles with various types of electron acceptors used for the explanation of the molecular mechanisms of biochemical processes are examined. The results of research by the authors on the synthesis of polymeric charge-transfer complexes based on 1-vinylindole, halogens, hydrogen halides, alkyl halides, halohydrins, chloranil, and organic derivatives of silicon and tin are correlated.

The intensive study of intermolecular donor–acceptor interactions began in the sixties. The detection in a number of charge-transfer complexes (CTC) of the properties of organic semiconductors and their ability to form intermediate structures in the course of a number of complex chemical reactions and biochemical processes [1-4] served as a stimulus for this research. It is known that the CTC are characterized by electron-density redistribution in the system leading to the appearance of a negative charge on the acceptor and a positive charge on the donor [5-11]. Each year the problem of the synthesis and properties of CTC more and more attracts the attention of researchers, as evidenced by the publication of a number of new reviews [12-16].

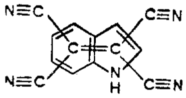
The study of CTC based on compounds of the pyrrole series is of particular significance because they are components of many natural substances. Of these compounds indole derivatives are worthy of the greatest attention in connection with their exceptionally important role in the physiological processes of plant and animal organisms. A number of studies carried out by various authors confirm the ability of indole derivatives to form CTC [17-19]. Szent-Györgi links the physiological activity of biologically active substances containing an indole ring with their electron-donor capacity [20].

Pullman and Pullman [18] in a correlation of research in quantum biochemistry point out that the electron-donor properties of pyrrole compounds increase, judging from the energy coefficients of their upper filled molecular orbitals, on passing from pyrrole to indole but remain unchanged on passing from indole to carbazole (Table 1).

In contrast to indole and tryptophan, serotonin (5-hydroxytryptamine) has a higher electron-donor capacity [21].

In 1961 Szent-Györgyi and Eisenberg [22] established the ability of indole and pyrrole to form colored stable complexes with iodine. In their opinion, transfer of an electron in this complex from the π system of indole to the iodine molecule occurs because of "local" interaction of I_2 with respect to the $C_{(2)}-C_{(3)}$ position of the indole ring, which has increased electron density [18, 23]. A study of the ESR spectra of indole introduced into 1,4-dibromobenzene crystals confirms localization of the spin density in the $C_{(2)}-C_{(3)}$ position [24].

Japanese [25] and American [26, 27] researchers have shown that alkyl- and arylpyrroles, as well as methoxyindoles, form CTC with chloranil and tetracyanoethylene (TCE), which absorb at 400-750 nm and have the properties of organic semiconductors. Sung and Parker [27] propose the following structure for the indole complex with TCE (λ_{max} 550 nm):



Foster [28] has established that the formation of an intermolecular CTC is an intermediate step in the reaction of indole with TCE, which leads to the final product – 3-tricyanovinylindole. Later Sidorov [29] made

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TABLE 1. Energies of the Orbitals of Pyrrole Compounds

Compound	Energy of upper filled molecular orbital	Energy of lower vacant molecular orbital
Pyrrole	0,618	−1,381
Indole	0,534	−0,863
Tryptophan	0,534	−0,863
Serotonin	0,461	—
Carbazole	0,539	−0,786

a spectral study of the complexing of metal derivatives of etioporphyrin with tetracyanoquinodimethane and TCE and showed that the π electrons of the tetrapyrrole ligand participate in the formation of the CTC. The reaction between a metalloporphyrin and Cl^-, Br^-, and I^- proceeds similarly; a bathochromic shift (10–20 nm) of all of the bands of the metalloporphyrin is observed in the spectra of the complexes with a simultaneous decrease in the intensity of the long-wave band [30].

Indole, tryptamine, and serotonin complexes with naphthalene, anthracene, biphenyl, and 1,1,4,4-tetraphenylbutadiene have been proposed in an American patent [31] for use in laser technology.

A number of papers on the study of the CTC of indoles with nitro derivatives are known. Foster [32] studied the molecular complexes of pyrrole and alkylindoles with 1,4-dinitrobenzene and 1,3,5-trinitrobenzene by means of NMR. Proceeding from the large chemical shifts of the 2-H and 3-H protons as compared with benzene ring protons, he assumed localization of the $\pi-\pi$ bond in the $C_{(2)}-C_{(3)}$ position of the pyrrole ring.

Sung and Parker [27] investigated the complexing of a number of different methoxyindoles with 1,3,5-trinitrobenzene and measured their association constants from PMR data. They showed that in the case of the formation of the indicated complexes the relative chemical shifts of the 3- and 4-H protons are larger than for the 2- and 7-H protons, respectively. Thus the following Δ^{D}_{DA} values (in hertz) were obtained for 5-methoxyindole: 2-H (27.0), 3-H (63.1), 4-H (95.4), and 7-H (63.6). The authors propose a structure with orientation of the donor and acceptor molecules in parallel planes for the molecular complexes. On the basis of the large association constants (K in kilograms per mole) for the 2-H (2.440) and 7-H (1.744) protons as compared with 3-H (1.573) and 4-H (1.412) they assume localization of the bond in the 2 and 7 positions during the formation of the CTC.

Colored crystalline indole and alkylindole complexes with 1-chloro- and 1-fluoro-2,4-dinitrobenzene have been obtained [33].

It has been shown by a study of the IR, UV, and PMR spectra of complexes of 2,3-substituted indoles with derivatives of di- and trinitrobenzenes that the formation and stability constants of CTC increase in conformity with the electron-donor capacity of indoles ($CH_3 > H \approx iso\text{-}C_3H_7 > C_2H_5 > tert\text{-}C_4H_9$) and the acceptor properties of nitrobenzene derivatives ($NO_2 > CN > COOCH_3 > H > CH_3 > OCH_3$) [34, 35]. The association constants of CTC between serotonin, tryptamine, dimethyltryptamine, and 1,3,5-trinitrobenzene have been determined by a spectrophotometric method [36].

Complexes of 12 indole derivatives of the 3-indolylacetic acid series with polynitrofluorenes have been described [37]. Compositions containing isoindole, 1,2,3-triphenylisoindole derivatives with 2,4,7-trinitrofluorenone are used in the manufacture of materials with improved electrophotographic sensitivity [38].

Kost and co-workers [39] have used the ability of indole derivatives to give CTC with electron-acceptor molecules for the separation of 3-(1-methylheptyl)indole into its optically active antipodes. (+)−α−(2,4,5,7-Tetranitro-9-fluorenylideneamino)propionic acid N-oxide, which reacts with 3-(1-methylheptyl)indole to give an optically active deeply colored black complex that absorbs at 440–470 nm, has been synthesized as an optically active acceptor.

The complexing of tryptophan with tetranitromethane [40] proceeds at a maximum rate at pH < 7.

Of the various electron acceptors in nature, quinones are widely distributed. Studies of the complexing of various indole compounds with quinones evidently make it possible to arrive at an understanding of the molecular mechanisms of biochemical processes. A spectral study of the CTC of indole, tryptophan, 5-hydroxytryptophan, and serotonin with benzoquinone, 2,6-dimethylbenzoquinone, and chloranil was carried out in liquid and supercooled solutions [41]. The complexes thus obtained give a strong ESR signal and coloration in aqueous solutions. A new method has been proposed for the identification of dimecarbine (1,2-dimethyl-3-carbethoxyindole) and mexamine (5-methoxytryptamine hydrochloride); this method is based on the formation of colored complexes with 1-nitroso-2-naphthol [42].

The preparation of complexes of tryptophan and other indole derivatives with various biochemical electron acceptors has been reported [43-52].

The enzyme nicotinamide adenine dinucleotide phosphate (NADP) plays an important role in most biological oxidation processes involving the transfer of electrons. There are numerous examples of its participation in intramolecular CTC. The most important compounds of this sort are compounds formed between NADP or related model compounds and derivatives of indole, serotonin, and tryptophan [44, 49-52, 53], which is the strongest electron donor of the four aromatic amino acids contained in proteins.

A reaction with π overlapping between indole and bases of nucleic acids, which leads to a hypsochromic effect in the electronic absorption spectra and fluorescent emission in aqueous solutions, has been investigated [54]. Model compounds in which indole and the bases of nucleic acids (adenine, cytosine, guanine, and thymine) are connected by trimethylene or tetramethylene bridges were synthesized for this purpose. For models of the indole$-(CH_2)_3-$base type the fraction of ordered configurations with π overlapping was estimated from the changes in the quantum luminescence yield and the lifetimes.

During a study of a number of cyclic amino acids and their derivatives as possible electron donors it was established that only those chemical compounds whose composition includes an indole ring have the ability to complex with riboflavin [44]. Bresler and co-workers [55] have investigated the processes involved in the formation and electrolytic dissociation of CTC between riboflavin, tryptophan, 5-hydroxytryptophan, and serotonin. The observed absorption at 400-500 nm attests to the formation of CTC. It was established that the bonding constants in the CTC and the activation energies depend on the chemical structure of the donor. Serotonin has the maximum degree of electron-donor properties, and tryptophan has the minimum degree. This regularity is explained by the presence in the serotonin molecule of a hydroxyl group in the 5 position of the indole ring, which increases its electronegativity. With respect to its electron-donor properties, 5-hydroxytryptophan lies between serotonin and tryptophan. It has been shown by ESR spectroscopy that the ability of the CTC to undergo dissociation to ion radicals is directly dependent on the electron-donor properties of indole derivatives. The equilibrium constant for the dissociation of the CTC in the case of 5-hydroxytryptophan is independent of the temperature, whereas the equilibrium constants for serotonin and tryptophan decrease as the temperature rises. The formation of indole complexes with other flavins in neutral and acidic solutions has been demonstrated by a spectrophotometric method [56, 57]. The appearance of bands with λ_{max} 500-550 nm is observed in the visible region of the spectra.

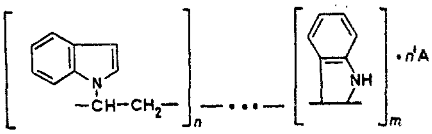
The formation of CTC from tryptophan and adenosine triphosphoric acid has been established [58]. The intermolecular donor—acceptor interaction of various indole compounds with thiamine (vitamin B_1) and thiamine pyrophosphate has been investigated by means of UV and NMR spectroscopy [59]. In analogy with the interaction of indole, tryptophan, and N^{α}-acetyltryptophan with acceptors of the phthalimide type in organic solvents [60], the formation of inter- and intramolecular CTC in polypeptides is assumed. All of the colored complexes give absorption maxima at 350-490 nm.

It has been established by pulse ^{19}F NMR that in the complexing of N-trifluoroacetyltryptophan with α-chymotrypsin the position of the resonance of the fluorine nuclei of N-trifluoroacetyltryptophan is shifted 1 ppm to weak field [61]. The constants of formation of complexes between indole or 1-tryptophan and α-cyclodextrin have been established by calorimetric titration [62]. The intermolecular interaction of indole and 3-methylindole with imidazole and histidine has been investigated by a spectrophotometric method [63, 64]. The same authors [63,64] used a similar method to detect CTC in some peptides and proteins containing tryptophan and histidine residues. The presence of an intramolecular singlet—singlet electron transition in indole alkaloids has been established by spectral methods [65].

It has been shown on the basis of PMR and mass spectral data that the protonated form of indole nitrogen-pyridylethylated tetrahydro-γ-carbolines forms CTC because of intramolecular interaction of the electron-donor indole and electron-acceptor pyridine systems [66].

Papers devoted to the study of complexing of indoles with the salts and organic derivatives of metals were published in 1974-1976. Thus it was established [67] that 1,3,3-trichloroisoindolenine forms complexes with $SbCl_5$ and $AlCl_3$. It was shown [68] that because of the formation of CTC, solutions of indole and $SbCl_3$ have electrical conductivity. The formation of complexes due to a donor—acceptor bond between Au^{3+} and the indole ring of tryptophan has been established spectrophotometrically [69]. The quenching of the fluorescence of indole by lanthanide ions is realized via a mechanism including electron transfer from the excited indole ring to the lanthanide ions [70]. The mass spectrometric behavior of trimethyl- and triphenyllead complexes with pyrrole and indole has been investigated [71].

The research on CTC based on indole and its derivatives has primarily encompassed the synthesis of low-molecular-weight complexes. The introduction of a vinyl group in the indole molecule opens up the possibility of the preparation and investigation of polymeric CTC. The first data on the synthesis of CTC from vinyl derivatives of indole pertain only to 1967-1968. Thus the polymerization of 1-vinylindole and 1-vinylpyrrole in the presence of tetracyanoethylene, chloranil, tetracyanoquinodimethane, and 1,4,5,8-tetrachloroanthraquinone, which proceeds through the intermediate formation of CTC, has been reported in a patent [72]. Polymeric CTC are formed by the reaction of 1-vinylindole and 1-vinylpyrrole with chloranil [73]. However, vinyl derivatives of imidazole and pyrrolidone form only monomeric complexes under similar conditions. A method for the preparation of polymeric complexes with 2,4,7-trinitro-9-fluorenone on the basis of poly(vinylindole) and a 1-vinylindole – indole copolymer, formed through an endocyclic double bond, has been patented [74, 75].



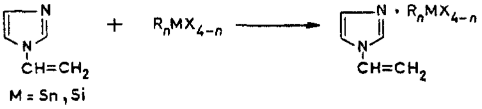
Kossmehl and Manecke [76] have investigated poly(vinylindole) as a catalyst for photochemical polymerization, using its ability to form an ion radical.

At the start of the sixties, Skvortsova and Domnina and co-workers did research on the chemistry of 1-vinylindole [77, 78]. They observed its ability to form CTC during an investigation of halogenation [79] and hydrohalogenation [80, 81]. The composition of the products depends on the amount of halogen introduced into the reaction. The determination of the molecular weights of the halogenation and hydrohalogenation products showed that they are mainly tetra-, hexa-, and octamers of halo derivatives of 1-vinylindole. Moreover, their degree of polymerization decreases as the amount of halogen used in the reaction is increased. The action of catalytic amounts of bromine, chlorine, iodine, and the corresponding hydrogen halides on 1-vinylindole gives rise to low-molecular-weight polymerization, the degree of which reaches 8-10%. Like halogens, catalytic amounts of alkyl halides, halohydrins, or chloranil also cause polymerization of 1-vinylindole [82]. 1-Vinylindole reacts with equimolar or excess amounts of these reagents to give brightly colored polymeric crystalline products with different compositions. Ethylene chlorohydrin, regardless of the amount used in the reaction, brings about only polymerization of 1-vinylindole. Trimethylene bromohydrin and 1,4-butylene chlorohydrin react considerably more vigorously to give colored polymeric products. Of the investigated acceptors, chloranil, which is incorporated in the composition of the polymer link in a ratio of 1 : 2, displays the greatest reactivity with respect to 1-vinylindole.

It has been established by pharmacological and microbiological studies of 1-vinylindole and complexes based on it that 1-vinylindole has a depressive effect on the central nervous system (CNS), prevents electrical shock- and karazol-induced convulsions, and excites respiration for a long time. The products of bromination of 1-vinylindole have a bacteriostatic effect on the tuberculosis bacillus. Chlorinated 1-vinylindole is active with respect to staphylococcus and diphtheria, sporogenous, and tuberculosis bacilli and has a fungistatic effect with respect to pathogenic fungi.

The dependence of the electrical properties of polymeric complexes on the electronic structure of ligands, the nature of the electron-acceptor component, and their ratio has been investigated.

Organylhalostannanes and organylhalosilanes have also been used as electron acceptors [82]. A detailed investigation of their reaction with 1-vinylazoles had been carried out previously [83, 84]. The formation of only monomeric complexes of different compositions through the unshared pair of electrons of the nitrogen atom in the 3 position and the vacant orbitals of the silicon and tin atoms was demonstrated:



The reaction of 1-vinylindole with organic derivatives of group IVB elements proceeds in a different direction. As in the case of stannic chloride [85], colored polymeric complexes with a small percentage of the acceptor are formed in the reaction of its organic derivatives with 1-vinylindole. Organic silicon compounds also bring about polymerization of 1-vinylindole. Of these compounds, trimethylchlorosilane, which forms a 4 : 1 complex, displays the highest activity.

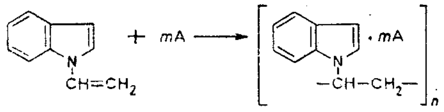
TABLE 2. ESR Spectra of Complexes Based on 1-Vinylindole (VI)

Investigated product	No. of unpaired electrons, N · 10^{-18} spins/g	Line width between the points of maximum slope ΔH, Oe
VI–bromine	12	11,3
VI–iodine	2,1	10
VI–chlorine	4,7	12,5
VI–HBr	20,0	12,5
VI–HCl	5,1	18,5
VI–C_2H_5Br	3,84	8
VI–propylene bromohydrin	6,82	13
VI–chloranil	7,44	6
VI–$C_6H_5SiCl_3$	2,1	9,5

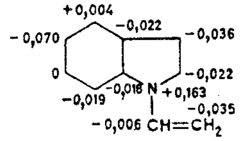
1-Vinylindoline and 1-vinyltetrahydroindole have been investigated as ligands to ascertain the complexing ability of vinyl derivatives of the indole series as a function of their electronic structure [86, 87]. They also form polymeric CTC with halogens, hydrogen halides, and organic electron acceptors.

The structures of the products of the reaction of 1-vinylindole with the investigated electron acceptors have been confirmed by means of physicochemical methods [79-82]. The polymeric character of the complexes based on 1-vinylindole was proved by the similarity between their IR spectra at 700-3600 cm^{-1} and the spectrum of individual poly(vinylindole). Bands of electron charge-transfer with maxima at 490-500 nm appear in the visible region of the spectra of the products of the reaction of 1-vinylindole, 1-ethylindone, and poly(vinylindole) with electron acceptors. The changes in the electronic spectra of 1-vinylindole complexes with halogens, hydrogen halides, and organic electron acceptors are independent of the amount of electron acceptor incorporated in the polymer chain. The intensity of the ESR signals for the investigated polymeric complexes correspond to the concentrations of the paramagnetic centers (on the order of 10^{18} per gram of the substance) (Table 2).

The set of all of the data obtained provides evidence that the products of the reaction of 1-vinylindole with halogens, hydrogen halides, and organic electron acceptors are polymeric charge-transfer complexes. The reaction proceeds through opening of the double bond of the vinyl group and donor–acceptor interaction of the indole rings of the polymer chain with the acceptor molecules.



The calculation of the 1-vinylindole molecule made by Frolov [88] within the Pople approximation provides evidence for increased π-electron densities on the β-carbon atom of the vinyl group and in the 2, 3, 6, and 8 positions of the indole ring.



The nitrogen atom has a positive charge, and its unshared pair of nσ electrons is delocalized over the entire system of π electrons. The donor–acceptor interaction of 1-vinylindole may therefore occur with the participation of the bonding molecular orbitals. According to the Mulliken classification [89], 1-vinylindole complexes with halogens, hydrogen halides, alkyl halides, and halohydrins should be of the πσ type, and the complexes with chloranil should be of the ππ type. The polymeric complexes of 1-vinylpyrrole with organylhalostannanes and organylhalosilanes formed with the participation of the vacant orbitals of tin and silicon are of the πν type.

The combination in the 1-vinylindole molecule of the properties of the vinyl monomer and the indole system ensures its ability to form high-molecular-weight charge-transfer complexes. Variation of the percentage and nature of the electron acceptor in them makes it possible to change their composition and properties.

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