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-Györgyi 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 I).

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 arylpyroles, 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 ($\lambda_{max}$ 550 nm):

![Indole complex with TCE](image)

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...
TABLE 1. Energies of the Orbitals of Pyrrole Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy of upper filled molecular orbital</th>
<th>Energy of lower vacant molecular orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrrole</td>
<td>0.618</td>
<td>-1.381</td>
</tr>
<tr>
<td>Indole</td>
<td>0.534</td>
<td>-0.863</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>0.534</td>
<td>-0.863</td>
</tr>
<tr>
<td>Serotonin</td>
<td>0.491</td>
<td>-0.863</td>
</tr>
<tr>
<td>Carbazole</td>
<td>0.539</td>
<td>-0.786</td>
</tr>
</tbody>
</table>

a spectral study of the complexing of metal derivatives of etioporphyrin with tetracyanoquinodimethane and TCE and showed that the π electrons of the tetrapyrorle 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 π-π 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 ΔDₐ 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 (CH₃ > H ≈ iso-C₂H₅ > C₂H₅ > tert-C₄H₉) and the acceptor properties of nitrobenzene derivatives (NO₂ > CN > COOCH₃ > H > CH₃ > OCH₃) [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-indolyacetic 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 enantiomers. (+)-α-β-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 tetrinitromethane [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...