CHARGE TRANSFER INTERACTION BETWEEN OFLOXACIN (SMR) AND SALICYLIC ACID (*SAA*) USING DENSITY FUNCTIONAL THEORY (*DFT*)

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This paper studies the new charge transfer complexes that were synthesized by equimolar mixing using sulfamethazine (SMR) as electron donor and aromatic and salicylic acid (SAA) as acceptor. The experiments were characterized by UV-Vis spectroscopy depicting electron microscopy (SEM). In addition, quantum chemical calculations performed at the DFT/B3LYP level of theory investigated the steady-state structure, energy and charge density of the complexes.

Keywords: donor; acceptor; antibiotic; DFT; complex; charge transfer

ИССЛЕДОВАНИЕ ВЗАИМОДЕЙСТВИЯ ПЕРЕНОСА ЗАРЯДА МЕЖДУОФЛОКСАЦИНОМ (*SMR*) И САЛИЦИЛОВОЙ КИСЛОТОЙ (SAA) С ИСПОЛЬЗОВАНИЕМ ТЕОРИИ ФУНКЦИОНАЛА ПЛОТНОСТИ (*DFT*)

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В данной работе исследованы новые комплексы с переносом заряда, синтезированные путем эквимолярного смешивания с использованием сульфаметазина (SMR) в качестве донора электронов и ароматической и салициловой кислоты (SAA) в качестве акцептора. Эксперименты характеризовались с помощью УФ-видимой спектроскопии и сканирующей электронной микроскопии (SEM). Кроме того, квантово-химические расчеты, выполненные на уровне теории DFT/B3LYP, исследовали стационарную структуру, энергию и плотность заряда комплексов.

Ключевые слова: дигмадонор; акцептор; антибиотик; DFT; комплекс; перенос заряда

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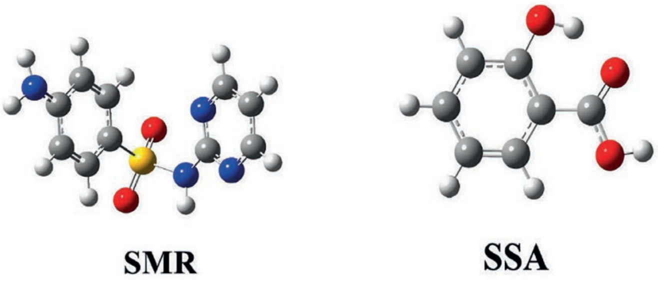
In charge transfer (CT) chemistry, electron-rich (electron-abundant) donor (D) molecules react with electron-poor (electron-deficient) acceptor (A) molecules. CT interactions between biological/drug compounds and small-molecule acceptors also have several applications [1]. Spectroscopic data helps to study the donor-acceptor mechanism and spectrophotometric titration determines the stoichiometric ratio[1]. Ultraviolet-visible (UV-Vis) and infrared (FTIR) spectroscopy analyzed the interaction mechanism, and scanning electron microscopy (SEM) observed the morphology of the complexes[2]. Finally, DFT calculations investigated the molecular geometry, binding energy and molecular orbitals.

Experimental section Sulfamethazine (SMR; C,,H,N,O,S; 264.30 g/mol) was obtained from Sigma-Aldrich Chemical Company, USA, with purity ≥98% (HPLC). Salicylic acid (SSA; 138.12 g/mol), were purchased from Sigma-Aldrich, USA, the structure of SMR and SSA show in Fig. 1.

Synthesis of the complexes The SMR and SSR solid CT complexes were prepared by mixing 1 mmol of SMR receptor and SSA solid (1 mmol) in methanol (10 ml) show in Fig. 2.

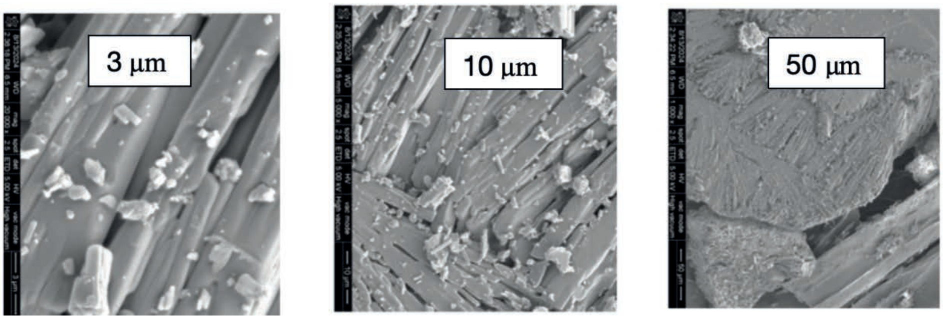
Quantum chemical calculations The title compound was optimized and validated using a density-functional theory (DFT) approach and the 6-31G* basis set.



a *b*

Fig. 1. The chemical structure of donor and acceptor:
*a – sul*famethazine (SMR); *b* – salicylic acid (SAA)

Results and Discussion Morphological characterization and FTIR spectroscopy SCNAning electron microscopy (SEM) helped to gain insight into the particle size, surface porosity and microstructure of the SAA-SMR complexes in table 1. The results show that the SAA-SMR complexes display a columnar structure with elongated pores that form adherent aggregates in fig 3. These structural differences between the complexes suggest that there may be significant differences in their physicochemical properties.



a *b* *c*

Fig. 2. SEM images of SAA-SMR complexes:
a – at 50 μm scales; *b* – at 10 μm; *c* – 3 at μm scales

DFT calculations Geometrical Parameters and Spectral Characteristics The geometry of the SMR -SSA complex was optimized under methanol conditions as shown in Fig. 3. The molecular geometry is determined by the balance of Coulombic attraction and repulsion between charged particles, both nuclei and electrons, leading to the lowest energy configuration on the potential energy surface [3].

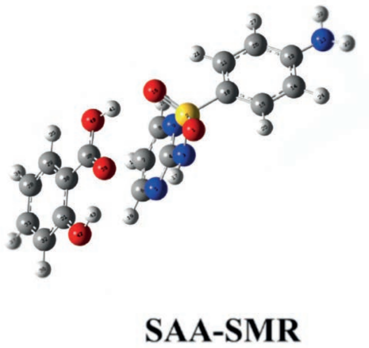


Fig. 3. Steady-state structure and atomic numbering of SAA-SMR complex

Energy Calculations The binding energies of such complexes were calculated as shown in Figure 4 to further understand their CT process. The binding energy of the SAA-SMR complex is -11.23 eV. The adsorption energies of both the acceptor and donor are negative, indicating that the complexation reaction between the donor and acceptor occurs spontaneously.

Table 1

FTIR wavenumbers (cm^{-1}) and tentative band assignments for SMR and their complexes

SMR	COA-SMR	CNA-SMR	SSA-SMR	Assignments
3456 s	3454 w	3493 w	3481 m	υ (N-H)
3354 m	3355 w	3352 s	3373 m	υ (N-H)
3243 s	3244 m	3244 w	3242 s	υ (+NH)
1654 s	1655 m	1672 m	1661 s	υ (C=O)
1593 m	1596 s	1605 s	1597 s	υ (C-C) in aromatic ring
1475 s	1477 m	1483 w	1481 s	υ(C-C) in ring
1347 s	1345 s	1327 w	1315 s	υ (C-N) in aromatic
1192 s	1215 m	1217 w	1211 w	C-H in-plane bending
1091 s	1087 w	1136 m	1153 s	υ (C-N)
977 m	972 w	975 w	977 w	NH2 Rocking
871 m	869 w	866 w	891 m	δ (C-H) para-substituted
688 m	687 m	690 m	692 m	N-H wagging band in secondary amide

s, strong; m, medium; w, weak; v, very; υ, stretching; δ, bending vibrations.

Similarly, the C-N structures in the SMR and the acceptor exhibited van der Waals forces (Fig. 4 .). In addition, the S-O group in SMR formed hydrogen bonds with the – COOH group in SAA. These findings, combined with FTIR spectroscopy (tabel 2), elucidated the mechanism of donor-acceptor complex formation.

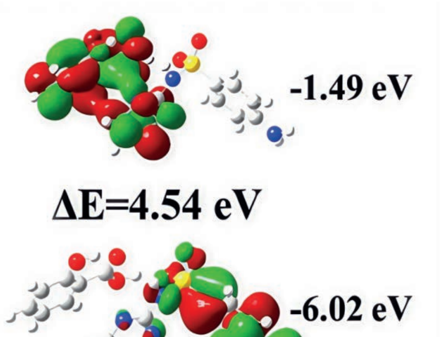


Fig. 4 .Binding energy of SAA-SMR substances

EHOMO and ELUMO analyses were performed on the SAA-SMR complexes as shown in Fig. 4 and tabel 2. The wave function results show that. For SAA-SMR complexes, Eномо and ELumo values were -6.02 e V and -1.63 eV, respectively, and Egap was 4.54 eV. Smaller Egap values for the complexes indicate higher chemical reactivity.

Table 2

The computed adsorption wavelength (nm), excitation energy (eV), absorbance and oscillator strengths (f) of the SAA-SMR complex by TDB3LYP/6-31G∗ method

Wavelength (nm)	Excitation Energy (eV)	Configurations composition	Oscillator Strength (f)	Transitions
333.33	3.7196	129 → 132 0.20093 129 → 133 0.11101 131 → 132 0.15436 131 → 134 0.64361	0.1539	n→δ∗
295.51	4.1956	128 → 133 -0.27178 129 → 132 0.39592 129 → 133 0.37870 130 → 134 0.20767 131 → 134 -0.18487 131 → 136 -0.11450	0.1915	n→δ∗
291.77	4.2494	128 → 133 -0.18742 129 → 132 -0.17027 129 → 133 -0.20362 129 → 134 0.10889 130 → 134 0.59326	0.1842	n→δ∗
288.41	4.2988	128 → 133 -0.20514 128 → 134 0.17917 129 → 134 0.59126 130 → 134 -0.20103	0.1063	n→δ∗
281.97	4.3971	128 → 134 0.67698 129 → 134 -0.14096	0.0568	n→δ∗

Mulliken analysis This analysis can be used to study the inter-bonding interactions as well as intramolecular and intermolecular bonding mechanisms . Table 1 lists the results of Mulliken atomic charge calculations for SAA-SMR complexes. In the SAA-SMR complex, the charges range from -0.763 and -0.762 in N3 to 1.253 in S2, respectively. These results indicate that O and N atoms tend to be negatively charged, while C and S atoms are positively charged. The atomic charge densities are more pronounced near the donor-acceptor region, suggesting that the conjugation interactions or charge transfer processes in these molecular systems are equivalent to donor-acceptor interactions between the non-Lewis NBO orbitals and the occupied Lewis NBO orbitals.

New charge transfer complexes were synthesized with sulfamethazine (SMR) as electron donor and salicylic acid (SAA) as electron acceptor. Through spectral analysis and DFT calculations, the results show that such compounds exhibit good reactivity tendencies as well as optimal positions for electrophilic and nucleophilic attack. The binding energies further indicate that these complexes are formed through a spontaneous reaction process. Key molecular interaction groups involved in charge transfer interactions were also identified. The C-N and N-H groups in the donor molecule and the -COOH group in the acceptor molecule play key roles in the complexation process.

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