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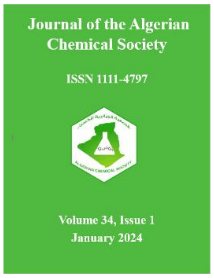

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Electronic characterization of a series of organic molecules and their charge transfer complexes using in silico approaches

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ABSTRACT

This work explored a series of organic molecules belonging to the tetrathiafulvalene (TTF) family and their charge transfer complexes (TTF-TCNQ), involving asymmetric molecules (donors) complexed with the acceptor molecule tetracyanoquinodimethane (TCNQ). This study was carried out by several in silico methods (molecular mechanics, DFT and PM3 . A structural study of the donors showed that the majority of the structures of these molecules are pseudo planar and exhibit Cs symmetry. The diagonal angles of the average planes of this series vary from 0.028° to 0.544°, with a calculation error of 0.001°. Charge transfer complexes (CTCs), which have a specific conductivity between 7.6 and 10.6 Ω -1 cm-1, correspond to a charge transfer between 0.61 and 0.72 e/mol and have a restricted gap of 1.58 to 1.71 eV, The computational results of electronic characteristics demonstrated strong correlation with experimental data.

Keywords: TTF, TCNQ, Organic material, Molecular mechanics, DFT, CT complex.

1. INTRODUCTION

The growing demand by researchers and the industrial world for materials intended for electronics and nonlinear optics has led chemists and physicists to develop theoretical concepts and experimental knowledge to propose compounds that are more efficient.

Organic compounds have long been known for their insulating properties. H.K. Onnes discovered superconductivity in 1911 [1].

The research boom started in 1973 when two American scientist groups reacted to the organic molecules TTF and TCNQ. The conductivity of the TTF-TCNQ material is 500 Ω^{-1} cm^{-1} at room temperature in the crystalline state [2].

In 1979, Danish researchers observed superconductivity within a TMTSF-DMTCNQ charge transfer complex [3,4]. The electrical conductivity of organic materials containing tetrathiafulvalene (TTF) or tetraselenafulvalene (TSF) π-donors depends on two factors, as shown by numerous theoretical [5-7] and experimental [8-10] studies. These factors include structural and electronic aspects.

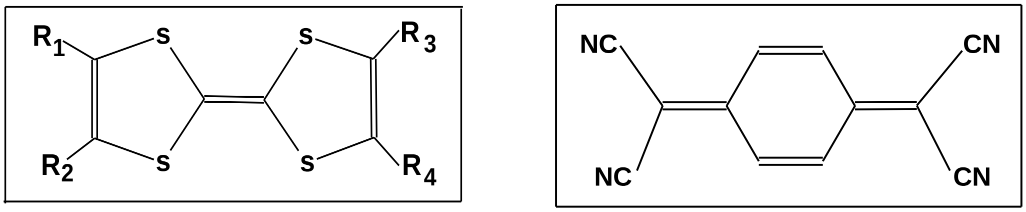
Molecular modelling encompasses all methods, theoretical and computational, used to model or mimic the behavior of molecules. These methods are used in the fields of computational chemistry drug design [11-16], computational biology and materials science to study molecular systems ranging from small chemical systems to large biological molecules and material assemblies. Molecular modelling methods are now used routinely to investigate the structure [17-22], structure/activity relationships [23-28], surface properties, polymeric systems, enzyme catalysis, DNA and membrane complexes.

This work explored a series of organic molecules belonging to the tetrathiafulvalene (TTF) family and their charge transfer complexes (TTF-TCNQ), involving asymmetric molecules (donors) complexed with the acceptor molecule tetracyanoquinodimethane (TCNQ).

2. COMPUTATIONAL METHODS

The current study aimed to determine the structures of donors and estimate the rate of charge transfer between π-donors (TTFs) and acceptors (TCNQs) based on experimental results [42-43]. Using molecular modelling, we propose studying the conformational and electronic properties of asymmetric donors from the family (TTF) and charge transfer complexes of the type TTF-TCNQ through calculations.

We propose to study the molecular modelling, conformational and electronic properties of the asymmetric π-donors of the TTF family (Fig.1a) with the TCNQ acceptor (Fig.1b) and the resulting CTCs of this association (TTF-TCNQ): R_1 = CH_3, CH_3S; R_2 = H, CH_3S; R_3 = C_6H_4OH, $C_6H_4OCOCH_3$; and R_4 = H, CH_3.



a **b**

Fig.1. Scheme of donors derived from tetrathiafulvalene (TTF) and scheme of the tetracyanoquinodimethane acceptor (TCNQ)

The investigation of the different preferred conformations of macrocycles and electronic calculations were carried out using molecular modeling software (molecular mechanics, DFT, semi-empirical methods: PM3 and extended Hückel theory: E.H.T.) and the following software: Gaussian 09 [44] and HyperChem (8.08) [45].

3. RESULTS AND DISCUSSION

3.1. Donor Energy Considerations

A conformational study is conducted based on the fundamental principles of molecular mechanics, as dictated by the following references [29-30]. The comparison of the relative stabilities of the different macrocycles studied is based on tension energy, while the thermodynamic stabilities of conformational isomers of the same compound will be compared using total steric energy [31-33]. For this analysis, HyperChem software is utilized, employing Kollman's choice of the AMBER force field [34].

The minimization algorithms used in the calculation of the preferred conformation were applied in the following order: steepest descent (the method of the greatest slope), conjugate gradient (conjugate gradient), and Newton–Raphson gradient. The calculation procedures terminate when they obtained minimum energy remains constant.

3.1.1. Variation in energy

In this series, the donors were studied using molecular mechanics (HyperChem/MM2) with the following calculation options: Dp-Dp, RFH, and SFC. Their cycles were as follows: M1 (R_1 = CH_3, R_2 = H, R_3 = C_6H_4OH, R_4 = H); M2 (R_1 = CH_3, R_2 = H, R_3 =C_6H_4OH, R_4 = CH_3); M3 (R_1 = CH_3, R_2 = H, R_3 = $C_6H_4OCOCH_3$, R_4 = H); M4 (R_1 = CH_3; R_2 = H, R_3 = $C_6H_4OCOCH_3$, R_4 = CH_3); M5 (R_1 = CH_3S, R_2 = CH_3S, R_3 = C_6H_4OH, R_4 = H), and M6 (R_1 = CH_3S, R_2 = CH_3S, R_3 = $C_6H_4OCOCH_3$, R_4 = H).

Figure 2 reveals that the tension energy of the M6 macrocycle is relatively high, with a value of 24.72 kcal/mol. In contrast, the M1 macrocycle exhibited an energy minimum with tension energy of 19.14 kcal/mol. The accuracy of the calculations for these values is within $\Delta E = 0.03$ kcal/mol. These results indicate a significant difference in tension energy between the two macrocycles, with M1 being the more stable conformation.

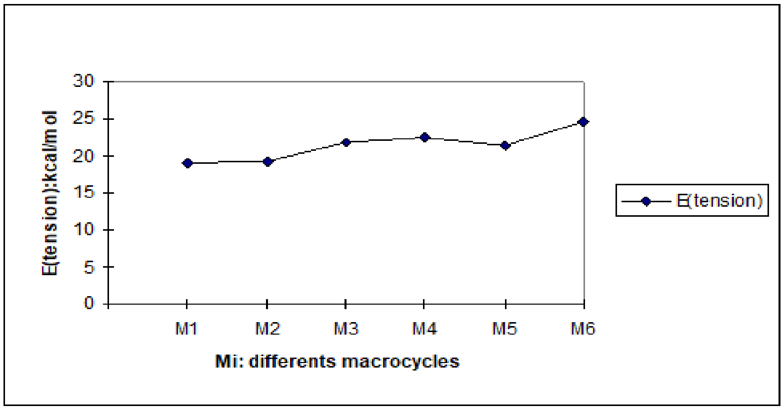


Fig.2. Diagram of the variation of the tension energy for the most stable conformations

The tendency for donor cyclization depends on the interactions and the resulting entropy change. The variation in the yield of the cyclization is parallel to that of the voltage energies of the different most stable macrocycles [35]. This result is in agreement with the experimental work on the yields of the reactions of the different π-donors [36].

3.1.2. Contributions of the different factors to the total steric energy

The minimum steric energy calculated using the molecular mechanics method (PCM/MM2) is determined by the sum of various energy contributions, including elongation energy (E(l)), bending energy (E(θ), torsion energy (E(ϕ)), van der Waals energy (E(VdW)), and electrostatic energy (E(elec)) [37].

$$E(Ste) = E(l) + E(\theta) + E(\phi) + E(VdW) + E(elec) \dots\dots\dots\dots (1)$$

We will undertake a review of their contributions and influences on total steric energy. In the specific case of the M6 macrocycle (as shown in Table 1), the contribution of torsion energy ($E(\phi)$) is significantly greater than that of van der Waals energy and bending stress.

Table 1. Contributions of the different factors to the total steric energy in kcal/mol

Macrocycle	M1	M2	M3	M4	M5	M6
steric energy	19,39	19,77	22,24	23,19	21,83	25,44
$E(l)$	00,52	00,34	00,42	00,37	00,36	00,39
$E(\theta)$	03,37	02,93	03,44	03,36	03,44	04,21
$E(\phi)$	07,58	10,92	10,91	13,43	12,07	14,15
$E(VdW)$	06,64	04,34	06,42	04,98	03,89	04,77
$E(elec)$	01,25	01,27	01,05	01,05	02,06	01,88

The torsion energy alone accounts for 55.62% of the total steric energy, with a value of 14.15 kcal/mol. This high contribution is primarily attributed to the presence of unfavorable torsion angles, as it is challenging to achieve perfectly staggered conformations for the majority of C-C bonds [38]. These molecules have very low conformational mobility compared to other macrolide-type macrocycles; indeed, in an energy window of 2 cal/mol, the majority of cycles have a single stable conformation [39, 40].

In conclusion, the torsional energy contribution appears to be the most significant factor among macrocycles examined in terms of their lowest-energy conformations. Eachmacrocycle compromises torsion, bending, and van der Waals energies, eventually adopting a conformation that corresponds to the minimum overall steric energy [27].

3.2. Geometric and Electronic Considerations

3.2.1. Geometric Study of Donors

We studied the structural parameters of macrocycle M1 in detail via the following formula (Fig.3).

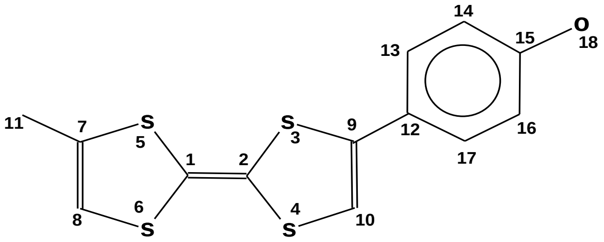


Fig.3. Detailed structure of the M1 macrocycle

The geometry of the M1 macrocycle exhibits Cs symmetry, as determined through a combination of molecular mechanics and density functional theory (DFT/B3LYP/6-31G) calculations (Fig.4.). The angle of the mean plane of the macrocycle (S5-S6-S3-S4) is nearly zero, with a value of 0.00105° according to the molecular mechanics calculations and 0.00241° according to the PM3 method. In addition, 0.193° according to DFT (as shown in Table 2). This confirms that the M1 macrocycle possesses a high degree of planarity. The distances between bonded atoms in the M1 macrocycle closely align with the reference values, as indicated in Table 2. We also note that the results of the calculations by the empirical semi empirical PM3 method and DFT are similar, molecular mechanics and the conformational study of functionalized and asymmetrically substituted π-donors derived from the tetrathiafulvalene family revealed that the predominant conformers of these molecules are nearly planar and possess Cs symmetry. The torsion angles of the mean planes of the different macrocycles ranged from 0.028° to 0.544°, with a high calculation precision of $\Delta\varphi = 0.001°$(as shown in Table3).

The presence of these nearly planar conformations can be attributed to the mesomeric effect between the parent TTF molecule and the functionalized groups. This mesomeric effect plays a significant role in stabilizing the conformations and influencing the geometry of the macrocycles, resulting in their observed planarity and Cs symmetry.

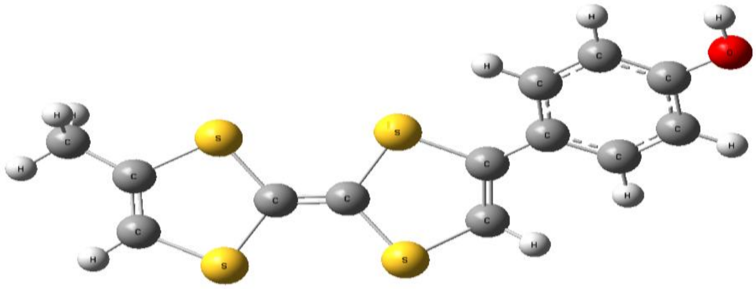


Fig.4. 3D structure of M1

Table 2. Distances between atoms in (Å) and Angles in degrees (M1)

distance	**MM**	**PM3**	**DFT/B3LYP /6-31G**	**Angle**	**MM**	**PM3**	**DFT/B3LYP /6-31G**
C1-C2	1,343	1,351	1.350	C1-C2-S3	121,582	122,538	123.425
C2-S3	1,803	1,763	1.781	C1-C2-S4	121,595	123,002	123.409
C2-S4	1,800	1,764	1.784	S5-C1-C2	121,453	122,747	123.520
C1-S5	1,808	1,763	1.783	S6-C1-C2	121,443	122,984	123.319
C1-S6	1,808	1,764	1.785	C1-S5-C7	092.312	095,402	95.397
S5-C7	1,800	1,763	1.781	C1-S6-C8	092.144	095,304	94.505
S6-C8	1,797	1,737	1.764	C2-S3-C9	093.549	095,414	95.304
C7-C8	1,329	1,346	1.340	S3-C9-C10	116,659	115,715	115.354
C7-C11	1,479	1,479	1.501	C2-S4-C10	092.362	095.158	94.430
S3-C9	1,814	1,769	1.789	S5-C7-C8	118,921	116,464	116.024
S4-C10	1,799	1,729	1.760	C9-C12-C13	119,929	121,097	121.498
C9-C10	1,338	1,352	1.346	C13-C14-C15	120,349	119,374	120.052
C9-C12	1,504	1,458	1.472	C8-C7-C11	121,831	124,372	126.471
C12-C13	1,413	1,399	1.404	S3-S4-S6-S5	0,00105	0,00241	000.193
C 13-C14	1,397	1,387	1.393	S5-C1-C2-S3	0,00082	0,00238	000.452
C14-C15	1,400	1,402	1.398	S6-C1-C2-S4	0.00127	0,00247	000.064
C15-C16	1,395	1,403	1.401	C1-S5-C7-C8	0.00362	0,01125	007.059
C16-C17	1,398	1,385	1.388	C1-S6-C8-C7	0,00388	0,00115	007.099
C12-C17	1,415	1,402	1.409	C2-S3-C9-C10	0.00832	0,00161	009.251
C15-O18	1,397	1,366	1.365	C2-S4-C10-C9	0.00681	0,01236	009.239

MM: Molecular Mechanics, PM3: Parametric Method 3, DFT: Density Functional Theory

Table 3. Values of torsion angles of the mean planes of stable conformations

Macrocycle	**M1**	**M2**	**M3**	**M4**	**M5**	**M6**
Torsion angle of the mean plane, in degree	0,088	0,028	0,120	0,544	0,082	0,260

3.2.2. Charge Transfer Complex (CTC)

The calculation of the charge transfer complex's energy gap was performed using the extended Hückel theory (E.H.T.) within HyperChem software. For non-metallic solids, the energy gap is related to the intrinsic conductivity through the following empirical relationship [41]:

$$\Omega = \Omega_0 \exp\left(\frac{\Delta\varepsilon}{2kT}\right)$$

A good correlation is observed between the theoretical and experimental values. Gouasmia et al. showed that powder complexes with significant conductivity, ranging from 7.6 to 10.6 Ω-1 cm-1, correspond to a charge transfer rate between 0.61 and 0.72 e/molecule. We have demonstrated that these complexes have a narrow energy gap (Δε) ranging from 1.58 to 1.71 eV (Table 4). This is in line with the reference value of 0.72 e/mol for HMTTF-TCNQ (hexamethylene-tetrathiafulvalene-tetra-cyano-quinodimethane). It is also noteworthy that for the M6-TCNQ complex, which has a relatively high-energy gap (Δε), the experimental determination of the charge transfer rate has failed [23].

Table 4. Electronic characteristics of charge transfer complexes

Charge Transfer Complex (CTC)	**Number of total orbitals**	**Number of Occupied orbitals**	**Δε (eV)**	**Charge transfer rate (exp.) e/molecule**	**Conductivity (exp.) Ω -1 cm-1**
M1-TCNQ	82	46	1,68	0,70	07,67
M2-TCNQ	88	49	1,71	0,72	01,36
M3-TCNQ	96	54	1,58	0,61	10,62
M4-TCNQ	102	57	1,62	0,66	10,00
M5-TCNQ	96	53	2,76	0,22	04 10^{-4}
M6-TCNQ	110	63	3,10	/	02 10^{-5}
HMTTF-TCNQ	76	42	1,47	0,72	26
TTF-TCNQ	44	26	1,42	0,59	15

Δε: ε LUMO-εHOMO : charge transfer band (HyperChem/E.H.T)

4. CONCLUSION

This research delved into the structural and electronic properties of a series of asymmetric tetrathiafulvalene (TTF) molecules and their charge transfer complexes (CTCs) with tetracyanoquinodimethane (TCNQ). Through a combination of in silico methods, including molecular mechanics, DFT and PM3, we gained valuable insights into the molecular geometries and electronic characteristics of these systems.

A conformational study of functionalized and asymmetrically substituted π-donors from the tetrathiafulvalene (TTF) family revealed that the majority of the preferred conformations of these molecules are nearly planar and exhibit Cs symmetry.

The introduction of functional groups and increased sulfur content in these new TTF derivatives leads to enhanced binding interactions between the diffuse π orbitals of sulfur and reduced Coulombic and torsional repulsion due to lower charge densities. These structural modifications result in improved interchain and intrachain contacts, which are crucial for promoting efficient charge transfer.

The formation of CTCs between the asymmetric TTF donors and TCNQ acceptor resulted in materials exhibiting significant electrical conductivity, ranging from 7.6 to 10.6 W^{-1} cm^{-1}. These conductivity values are associated with charge transfer rates between 0.61 and 0.72 electrons per molecule and a restricted energy gap of 1.58 to 1.71 eV.

These findings suggest that some of these newly developed molecules exhibit excellent donor-π interactions, making them promising candidates for the development of organic conductors.

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