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Molecular Modelling of New Materials from the Tetrathiafulvalene Family

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The structural and electronic study of new molecular materials from the tetrathiafulvalene family were analyzed and compared by using molecular modelling (molecular mechanics, molecular dynamics, complete neglecting of differential overlapping and the extended Hückel theory. The good correlations between the calculated and experimental values are presented.

Key Words: Molecular material, Tetrathiafulvalene, TCNQ, Charge transfer, Molecular mechanics, Extended Hückel theory.

INTRODUCTION

The construction of lattices created from molecular building blocks has been the focus of considerable synthetic[1–4] as well as theoretical endeavour[5–8] over the last twenty years. The potential for the incorporation of unusual electrical, magnetic, optical and structural properties in materials that can display very different features compared to conventional continuous lattices has driven this effort. One area that has provided many examples of materials with varying physical properties are charge transfer complexes.

In the present work, the structure of the donors and estimated the degree of charge transfer between the donors of type tetrathiafulvalene (TTF) and the acceptors tetracyanoquinodimethane (TCNQ) are determined .

The calculations were made by using molecular modelling, the conformational and electronic properties of the donors derived from the TTF family and their complexes of type (TTF-TCNQ) (Figs. 1a, 1b), with $R_1 = C_6H_4OH$, $C_6H_4OCOCH_3$; $R_2 = R_2' = CH_3$; $R_2—R_2' = (CH_2)_3$; $(CH_2)_4$; $(HC{=}CH)_2$.

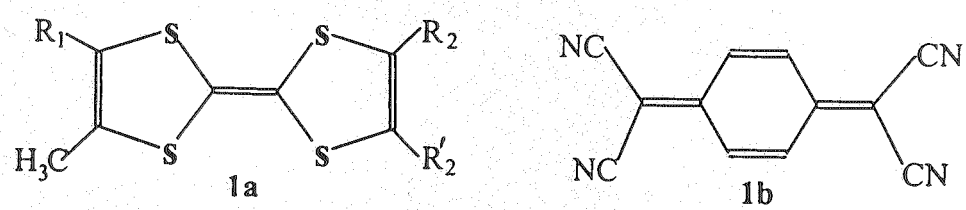

Fig. 1. Scheme of the *p*-donors based on TTF (**1a**) and the TCNQ acceptor (**1b**)

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EXPERIMENTAL

Calculations were carried out using molecular modelling, with three software packages: PCM (6.1)[9] used for geometry optimization and calculation of energies, HyperChem (7.01)[10] used for conformational search and calculation of degree transfer charge and Chem 3D (7.0)[11] used for structural representation.

The minimum energy geometries were located by minimizing energy with respect to all geometrical coordinates and without imposing any symmetry constraints. The molecular mechanics (PCM) is a method for structure determination, which uses a quantum mechanical (VESCF) Π-system calculation in the iterative sequence and Allinger's MM2 force field[12]. These calculations use the "Monte Carlo" simulations and the Metropolis algorithm[13].

The minimization algorithms used repeatedly in the calculation of the privileged conformation are in the following order: steepest-descent, conjugated gradient and Newton-Raphson. The calculation procedures were stopped when the minimal energy obtained became constant.

The molecular dynamics (HyperChem) for the conformational research are also used, with the following options: 1000 K, *in vacuo*, step size: 0.001 ps, relaxation time: 0.1 ps. Based on these calculations and the Boltzmann distribution[14], the aim is to find all these low-energy conformers.

RESULTS AND DISCUSSION

Energetic considerations

Variation of the total strain energy: The conformational study is based on molecular mechanics. The calculation of energy has been calculated by the PCM software, with the following options: dipole-dipole (dp-dp), self-consistent field (SCF), restricted Hartree-Fock (RHF). The entire steric energy is used to compare the thermodynamic stability of conformational isomers of the same compound. The strain energy is used for a comparison of the relative stability of different studied macrocycles[15, 16]. Fig. 2 presents an evolution of the strain energy as a function of the mass for different macrocycles.

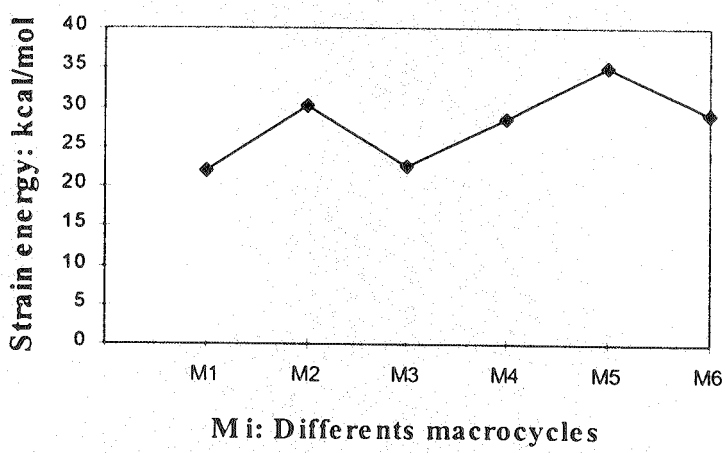

Fig. 2. Evolution of the strain energy for different macrocycles

The strain energy is relatively higher for M_5 macrocycle (E(st/n) = 35.20 kcal/mol) and a minimum energy for the M_3 (E(ten) = 22.48 kcal/mol), with a precision on the calculation of 0.03 kcal/mol. In line with the above conclusions, the rate of cyclization increases with the size of the ring[17]. This is in good agreement with our results, which indicate an evolution of strain energy opposite to the size of the ring.

Contributions of different features to steric energy: The steric energy was calculated[14] from the sum of different contributions such as stretching, bending, torsional, van der Waals and electrostatic energies:

$$E(steric) = E(stretch) + E(bend) + E(tors) + E(VdW) + E(electr) \quad (1)$$

We have investigated their contributions and influences on steric energy (Table-1).

TABLE-1
CONTRIBUTIONS OF DIFFERENT FEATURES TO STERIC ENERGY

Macrocycle	M_1	M_2	M_3	M_4	M_5	M_6
Steric energy	22.64	34.55	24.86	29.55	37.16	31.76
E(l)	00.40	00.43	00.52	00.54	00.98	00.67
E(θ)	04.00	03.97	03.92	05.05	10.50	05.58
E(ϕ)	11.81	22.08	12.36	14.71	16.94	14.61
E(VdW)	01.97	03.74	03.67	03.09	02.70	04.66
E(elcc)	04.45	04.37	04.35	06.19	06.22	06.23

In the particular case of the M_2 macrocycle, the torsional energy contribution (E(ϕ) = 22.08 kcal/mol) is distinctly greater than that of van der Waals and bending contribution represents 63.9% of the total steric energy. This is essentially due to unfavourable torsional angles because it is not possible to obtain the perfectly altered conformation of a majority of C—C bonds, as in the case of other macrocycles.

In conclusion, the contribution of the torsional energy is higher in all examined macrocycles in their stable conformers. In each ring, the minimum total energy is a compromise between the torsional, bending and van der Waals energies[18].

Geometrical and electronic considerations

Geometrical study: The conformation searching operation was as follows: a crude starting geometry is produced and its structure is optimized by molecular mechanics energy minimization. The resulting minimum energy conformer is then compared with previously found conformers to test for possible duplication. If the conformer thus generated is a previously undiscovered one, it is added to an accumulating list of unique conformers and the cycle is then repeated by obtaining a new crude starting geometry energy minimization, etc. When all given starting geometries have been used or when new minima cease to be found, the search is terminated. This is in agreement with Still's work[19].

The structural parameters of the M_2 macrocycle is studied in detail, which possesses the most elevated conductivity and the lowest gap (Fig. 3).

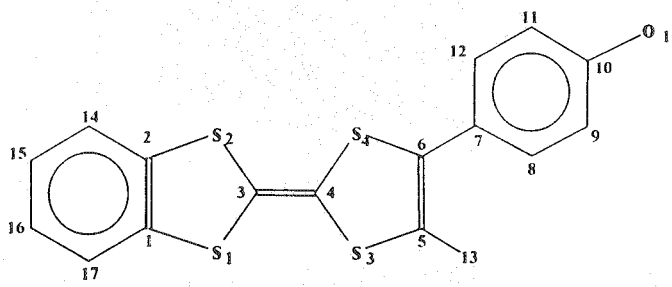

Fig. 3. Detailed scheme of the M_2 macrocycle

The geometry of the M_2 macrocycle presents a Cs symmetry obtained by a molecular mechanics calculations and a refinement by the molecular dynamics, with the options of the following calculation: *in vacuo*, step size 0.001 ps, relaxation time 0.1 ps; the conformation is stabilized to 298.75 K (Fig. 4). The angle of the average plane of the macrocycle (S1-S2-S4-S3) is almost equal to zero, it is of 0.123° according to the calculation of the molecular mechanics and of 0.128° according to the calculation of the CNDO method (Table-2); the options of the CNDO calculations, spin multiplicity: 1, spin pairing: RHF, state: lowest. These results confirmed that M2 macrocycle has a planar structure.

The values of the distances between linked atoms are very close to the values of references (Table-2). The charge of the atoms varies between –0.2365 for the oxygen and 0.1327 for the hydrogen of the hydroxyl group. The similarity of results between the calculations by molecular mechanics and CNDO method is observed and the gaps vary from 0.0085–0.0911 for the distances and from 0.003–7.701° for the angles.

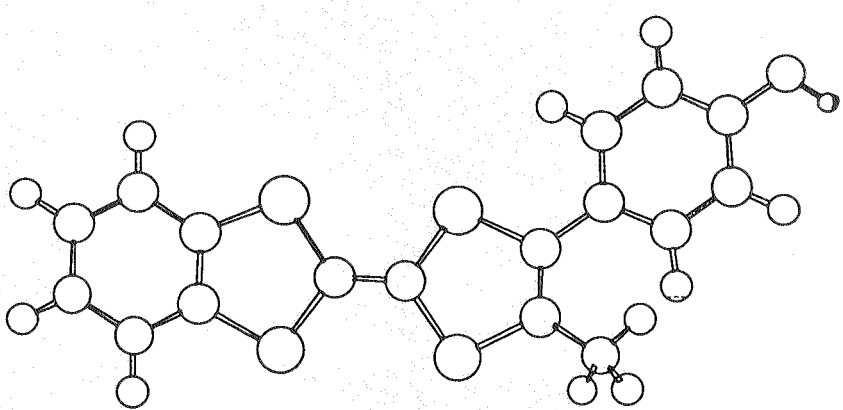

Fig. 4. Structure of the M_2 macrocycle

The conformational study of the π-donors asymmetrically substituted of the tetrathiafulvalene family showed that the average planes of the privileged conformers which constituent these molecules are near to the value zero. The torsional angles of the average planes of the different macrocycles vary between

0.081° (M_5) and 0.313° (M_1), with a precision on the calculation of 0.001°. It is mainly due to the mesomere effect, between the TTF molecule and the functionalized groups.

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°)

Atoms (a-b)	Length (MM)	Length (CNDO)	Atoms (a-b-c)	Angle (MM)	Angle (CNDO)
C1-C2	1.3465	1.3804	S1-C3-C4	128.094	124.066
C1-S1	1.8330	1.8696	S2-C3-C4	127.149	123.482
C2-S2	1.8311	1.8694	C3-C4-S4	128.180	124.945
S2-C3	1.8194	1.8650	S2-C3-S1	104.752	112.453
C3-C4	1.3309	1.3015	S4-C4-S3	102.263	110.106
S1-C3	1.8194	1.8644	S2-C2-C1	114.731	117.359
C4-S4	1.8049	1.8604	C2-S2-C3	102.894	096.394
C4-S3	1.8063	1.8612	C1-S1-C3	102.790	096.379
S4-C6	1.8476	1.8868	C2-C1-S1	114.830	117.404
S3-C5	1.8438	1.8792	C2-C14-C15	118.343	118.481
C5-C6	1.3621	1.3315	C6-C5-C13	129.358	131.023
C6-C7	1.3576	1.4487	C6-C7-C8	124.936	121.720
C7-C8	1.3485	1.3992	C7-C8-C9	123.372	123.492
C8-C9	1.3429	1.3812	C9-C10-O1	121.788	118.249
C9-C10	1.3402	1.3924	S1-S2-S4-S3	000.123	000.128
C10-O1	1.3595	1.3677	S2-C3-C4-S4	000.105	000.115
C2-C14	1.3394	1.3803	S1-C3-C4-S3	000.137	000.140
C14-C15	1.3434	1.3859	S2-C3-C4-S3	179.298	179.918
C15-C16	1.3448	1.3847	S1-C3-C4-S4	179.055	179.827
C16-C17	1.3437	1.3859	S1-C3-S2-C2	000.425	000.977

MM: Molecular mechanics, CNDO: Complex neglecting of Differential overlapping.

These macrocycles have a weak conformational mobility, with regard to the other macrocycles of macrolide type. In a window of 2 kcal/mol, only two privileged conformations are found[20–23].

Electronic study: The calculation of the gap for the complexes of charge transfer has been realized by the EHT method of the software HyperChem for the solid non-metallic; the gap is bound to the intrinsic conductivity by the following empiric relation[24]:

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

Gouasmia *et al.*[1, 5] showed that the powder complexes that have a specific conductivity between 1 and 11 S cm^{-1} correspond to a rate of charge transfer between 0.61 and 0.74 e/molecule. We showed that they have a HOMO/LUMO gap very restricted of 0.19–0.29 eV (Table-3). There is a good agreement with the reference value of 0.72 e/molecule for HMTTF-TCNQ.

TABLE-3
ELECTRIC CHARACTERIZATIONS OF THE CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes	Number of total orbitals (s, p, d)	Number of occupied orbitals	Energy gap Δε (calculated) (eV)	Rate of charge-transfer (exp.) (e/molecule)	Electrical conductivity (exp.) (S cm^{-1})
M_1-TCNQ	114	52	0.33	0.36	3.5×10^{-5}
M_2-TCNQ	120	55	0.19	0.74	11
M_3-TCNQ	124	57	0.32	0.38	5.5×10^{-5}
M_4-TCNQ	128	60	0.29	0.66	04
M_5-TCNQ	132	62	0.25	0.61	01
M_6-TCNQ	138	65	0.27	0.70	03
HMTTF-TCNQ	96	42	0.20	0.72	26
TTF-TCNQ	64	26	0.28	0.59	15

$\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO}$ (HyperChem/EHT).

Conclusion

The study of new molecular materials, belonging to the family of charge transfer complexes (TTF-TCNQ) implying asymmetrical donors, was performed by molecular modelling. The conformational study of the donors showed that the majority of the constituent privileged conformers of these molecules are practically pseudo-planars. The torsional angles of the average planes of the different macrocycles vary between 0.081° and 0.313°.

The more the enrichment in sulfur of the new donors of the family TTF permitted, the more diffused the multiplication of the binding interactions between the orbitals of sulfur and less the Colombian torsional repulsion.

A good correlation between the theoretical values and the experimental values was obtained. The complexes that have a specific conductivity between 1 and 11 S cm^{-1} correspond to a charge transfer degree between 0.61 and 0.74 e/molecule and have a very restricted gap from 0.19 to 0.29 eV.

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