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Theoretical Characterization of New Organic Compounds Derived From Tetrathiafulvalene

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Theoretical study of new organic compounds derived from the tetrathiafulvalene (TTF) family, was performed by molecular modeling (molecular mechanics, molecular dynamics; PM3 and EHT). A good correlation between the theoretical and the experimental values were obtained. The complexes have a specific conductivity between 0.1 and 150 S cm^{-1} correspond to a charge transfer degree between 0.38 and 0.82 e/molecule and have a very restricted HOMO/LUMO gap from 0.108 to 0.128 eV.

Key Words: Tetrathiafulvalene, Tetracyanoquinodimethane, Charge transfer, Molecular mechanics, PM3, EHT.

INTRODUCTION

During the past few years, a considerable research effort has been focused upon the synthesis of more sophisticated tetrathiafulvalenes[1-5], as well as theoretical study[6-10]. Tetrathiafulvalene (TTF) and its derivatives have been extensively studied due to their unique electron-donating properties[1]. In addition to the famous intermolecular charge transfer complexes related to organic metals and electrically conducting materials, TTF has been covalently linked to various electron-acceptor moieties[11].

In the present work, the structure of the donors and estimated degree of charge transfer between the donors tetrathiafulvalene (TTF) and the acceptors tetracyanoquinodimethane (TCNQ) are determined. The calculations were made by using the molecular modeling, the conformational and electronic properties of the donors, derived from the TTF family and their complexes of type (TTF-TCNQ) (Figs. 1a and 1b).

EXPERIMENTAL

Calculations were carried out using molecular modeling, with 3 software packages. PCM (6.5)[12] used for geometry optimization and calculation of energies. HyperChem (7.5)[13] used for conformational search and calculation of degree transfer charge and Chem 3D (8.0)[14] used for structural representation.

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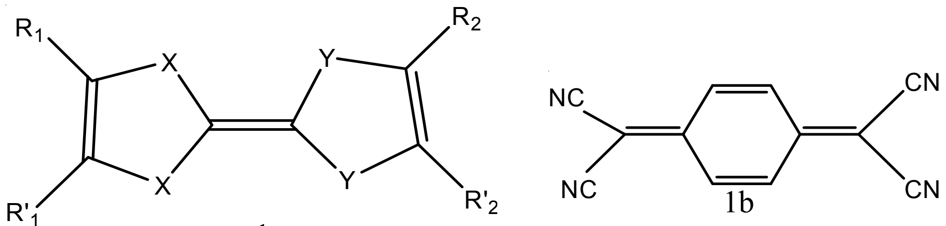

1a

1b

M1: R_1-R'_1 = $(CH_2)_4$; R_2-R'_2 = $(CH_2)_4$; X=Y= S
M2: R_1-R'_1 = $(CH_2)_3$; R_2-R'_2= $(CH=CH)_2$; X= Se and Y=S
M3: R_1-R'_1 = $(CH_2)_4$; R_2-R'_2= $(CH_2)_3$; X= Se and Y=S
M4: R_1-R'_1 = $(CH_2)_3$; R_2-R'_2= $(CH_2)_4$; X= Se and Y=S
M5: R_1-R'_1 = $(CH_2)_4$; R_2-R'_2= $(CH=CH)_2$; X= Se and Y=S
M6: R_1-R'_1 = $(CH_2)_3$; R_2-R'_2= $(Se)_2$-CH_2; X= Se and Y=S
M7: R_1-R'_1 = $(CH_2)_3$; R_2-R'_2= $(Se$-$CH)_2$; X= Se and Y=S

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

The minimum energy geometries were located by minimizing energy with respect to all geometrical coordinates and without imposing any symmetry constraints. The molecular mechanics 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[15]. These calculations use the 'Monte Carlo' simulations and the Metropolis algorithm[16].

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 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[17], 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: dp-dp (dipole-dipole), SCF (Self-Consistent Field), RHF (Restricted Hartree-Fock). 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[18,19]. Table-1 presents an evolution of the strain energy as a function of the mass for different macrocycles.

TABLE-1
STRAIN ENERGY AS A FUNCTION OF THE MASS FOR DIFFERENT MACROCYCLES

Macrocycle	M1	M2	M3	M4	M5	M6	M7
E (kcal/mol)	7.45	27.97	13.37	13.36	22.10	21.39	14.11

The strain energy is relatively higher for M2 macrocycle (E (st/n) = 27.97 kcal/mol) and a minimum energy for the M1 (E (ten) = 7.45 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[20]. This is in good agreement with present results, which indicate that an evolution of strain energy is opposite to the size of the ring.

Contributions of different features to steric energy: The steric energy was calculated from the sum of different contributions such as stretching, bending, torsional, van der Waals and electrostatic energies[19]:

$$E\ (\text{steric}) = E\ (\text{stretch}) + E\ (\text{bend}) + E\ (\text{tors}) + E\ (\text{vdw}) + E\ (\text{electr}) \qquad (1)$$

We have investigated their contributions and influences on steric energy (Table-2).

TABLE-2
CONTRIBUTIONS OF DIFFERENT FEATURES TO STERIC ENERGY (kcal/mol)

Macrocycles	M1	M2	M3	M4	M5	M6	M7
E (total)	11.72	29.69	17.17	17.16	24.26	23.86	26.24
E (l)	0.56	0.75	0.87	0.88	0.43	0.79	0.77
E (θ)	3.91	80.74	9.31	9.26	3.20	11.77	9.50
E (φ)	0.13	15.39	1.96	2.01	13.72	2.17	2.61
E (vdw)	3.01	0.57	0.89	0.88	2.73	-1.03	3.57
E (elect)	4.11	4.24	4.14	4.13	4.18	10.16	9.76

In the particular case of the M2 macrocycle, the torsional energy contribution ($E(\phi)$ = 15.39 kcal/mol), is distinctly greater than that of van der Waals and bending contribution, which represents 52.25 % 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[21].

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[21].

The structural parameters of the M3 macrocycle is studied in detail, which possesses the most elevated conductivity (Fig. 2).

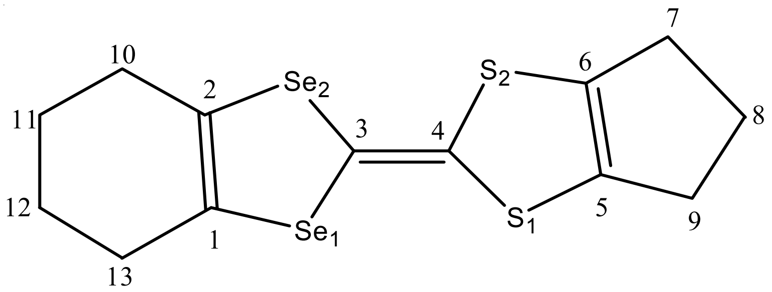

Fig. 2. Detailed scheme of the M3 macrocycle

The geometry of the M3 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 336 K (Fig. 3). The angle of the average plane of the macrocycle (Se1-Se2-S2-S1) is almost equal to zero, it is of 0.060° according to the calculation of the molecular mechanics and of 0.072° according to the calculation of the PM3 method (Table-3); the options of the PM3 calculations, spin multiplicity: 1, spin pairing: RHF, state: lowest. These results confirmed that M3 macrocycle has a pseudo-planar structure.

The charges of the atoms vary between -0.84423 for the selenium 1 and 0.30982 for the carbon 13. The similarity of results between the calculations by molecular mechanics and PM3 method is observed and the gaps vary from 0.00094-0.08507 Å for the distances and from 0.012-11.124° for the angles.

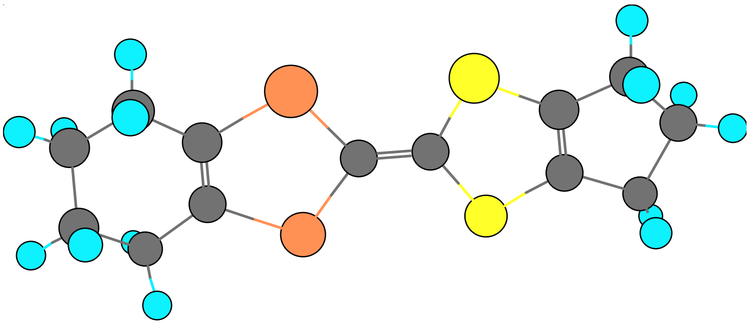

Fig. 3. Structure of the M3 macrocycle (Chem 3D)

TABLE-3
SELECTED BOUND LENGTHS IN ANGSTROM AND
SELECTED ANGLES IN DEGREES

Atoms a-b	Length (MM)	Length (PM3)	Atoms a-b-c	Angle (MM)	Angle (PM3)
C1-Se1	1.89445	1.88552	Se1-C3-C4	121.977	131.881
Se1-C3	1.88802	1.83382	Se2-C3-C4	121.797	115.161
C2-Se2	1.89377	1.88283	C3-C4-S1	127.379	127.745
Se2-C3	1.88777	1.86308	C3-C4-S2	127.219	116.095
C4-S1	1.82926	1.75189	C1-Se1-C3	89.221	95.727
S1-C5	1.82505	1.74110	C2-Se2-C3	88.972	95.641
C4-S2	1.82921	1.77284	C4-S1-C5	101.974	93.106
S2-C6	1.82463	1.73956	S1-C5-C6	115.521	118.741
C1-C2	1.34508	1.32263	S2-C6-C7	131.128	129.965
C3-C4	1.33691	1.32835	Se1-C1-C2	119.328	118.331
C5-C6	1.33646	1.35810	Se2-C2-C1	119.426	117.334
C6-C7	1.49220	1.49073	C1-C2-C10	123.115	124.884
C7-C8	1.56288	1.54131	C5-C6-C7	113.343	112.188
C8-C9	1.56301	1.54122	Se1-Se2-S2-S1	0.060	0.072
C9-C5	1.49235	1.49141	Se1-C3-C4-S1	0.196	0.204
C2-C10	1.50929	1.47173	Se2-C3-C4-S2	0.192	0.236
C10-C11	1.54598	1.52779	Se1-S3-C4-S2	176.340	179.887
C11-C12	1.54479	1.52396	Se2-C3-C4-S1	176.345	179.673
C12-C13	1.54655	1.52759	C2-C1-Se1-C3	11.449	0.388
C13-C1	1.51032	1.47177	C6-C5-S1-C4	0.872	0.203

MM: Molecular Mechanics.

The conformational study of the π-donors asymmetrically substituted of the tetrathiafulvalene family showed that the average planes of the privileged conformers are near to the zero value. The torsional angles of the average planes of the different macrocycles vary between 0.03° and 0.07°, 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.

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[22-26].

Electronic study: The calculation of the gap for the complexes of charge transfer has been realized by the EHT method (HyperChem) for the solid non-metallic. The gap is bound to the intrinsic conductivity by the following empiric relation[27]:

$$\Omega = \Omega_o \exp\left(-\Delta\varepsilon / 2KT\right) \qquad (2)$$

Gouasmia *et al.*[3,5] showed that the powder complexes that have a specific conductivity between (0.1 and 150 S cm^{-1}) correspond to a rate of charge transfer between 0.38 and 0.82 e/molecule. We showed that they have a HOMO/LUMO gap restricted of 0.108-0.128 eV (Table-4). There is a good agreement with the reference value of 0.72 e/molecule for HMTTF-TCNQ.

TABLE-4
ELECTRIC CHARACTERIZATIONS OF THE CHARGE-TRANSFER COMPLEXES

Charge-transfer complexes (CTC)	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})
M1-TCNQ	108	48	0.133	–	10^{-5}
M2-TCNQ	88	43	0.134	0.24	10^{-5}
M3-TCNQ	92	45	0.128	0.82	150
M4-TCNQ	92	45	0.116	0.38	0.1
M5-TCNQ	94	46	0.209	0.29	10^{-5}
M6-TCNQ	92	42	0.177	–	8.5×10^{-6}
M7-TCNQ	98	45	0.108	–	0.6
HMTTF-TCNQ	96	42	0.200	0,72	26
TTF-TCNQ	64	26	0.280	0,59	15

$\Delta\varepsilon = \varepsilon_{LUMO} – \varepsilon_{HOMO}$ (HyperChem/E.H.T).

Conclusion

The study of new organic compounds, belonging to the family of charge transfer complexes (TTF-TCNQ) implying asymmetrical donors, was performed by molecular modeling. The conformational study of the donors showed that the majority of the privileged conformers are practically pseudo-planars. The torsional angles of the average planes of the different macrocycles vary between 0.03° and 0.07°.

The more enrichment in sulfur and selenium of the new donors of the family TTF permitted more binding interactions between the orbitals of sulfur and selenium and less the colombian torsional repulsion.

A good correlation between the theoretical and the experimental values were obtained. The complexes that have a specific conductivity between 0.1 and 150 S. cm^{-1} correspond to a charge transfer degree between 0.32 and 0.824 e/molecule and have a restricted HOMO/LUMO gap from 0.108 to 0.128 eV.

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