Molecular dynamics of catenanes and molecular machines of nonbiological nature

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What is molecular machine?

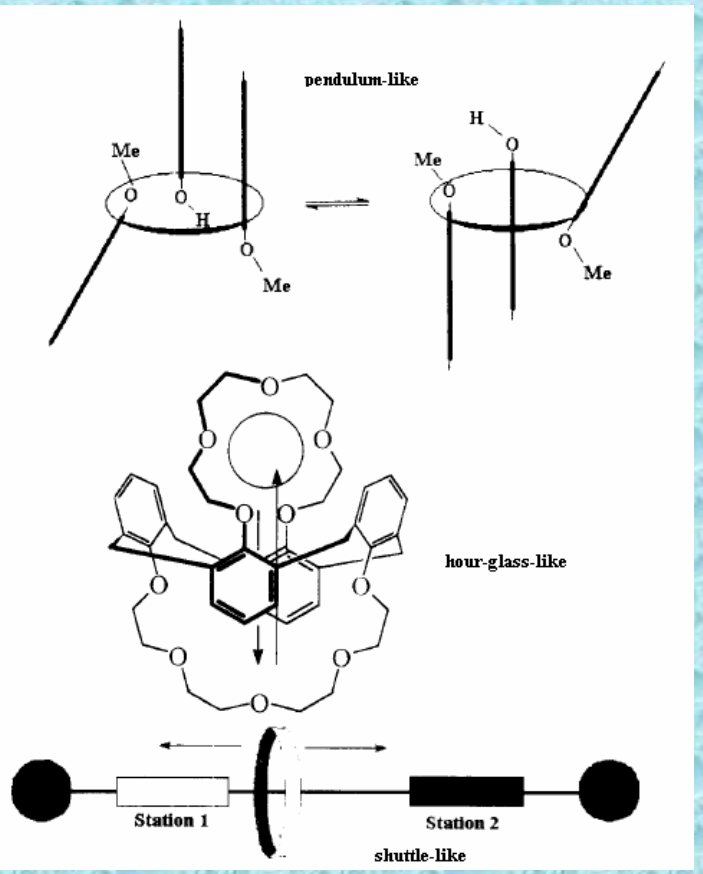
In the present paper being read we will deal only with molecular-sized systems exhibiting *mechanical* properties interpretable in terms of *classical mechanics*. In other words, molecular machines mentioned below are meant to be such molecular systems that use conformational mobility for functioning.

Like macroscopic machines, molecular-level ones are characterized by

- the kind of energy input supplied to make them work
- the kind of movement performed by their components
- the way in which their operation can be monitored
- the possibility to repeat the operation at will
- the time scale needed to complete a cycle of operation
- the function performed

At the moment the following types of molecular machines and constructions are known and described:

- “propellers” and “gear wheels”
- “brakes” and “turnstiles”
- “pendulums” and “hour-glasses”
- “gyroscopes”, “rotors” and “mills”
- “shuttles”



Z. Asfari and J. Vicens,
Journal of Inclusion Phenomena and Macrocyclic Chemistry **36** (2000).
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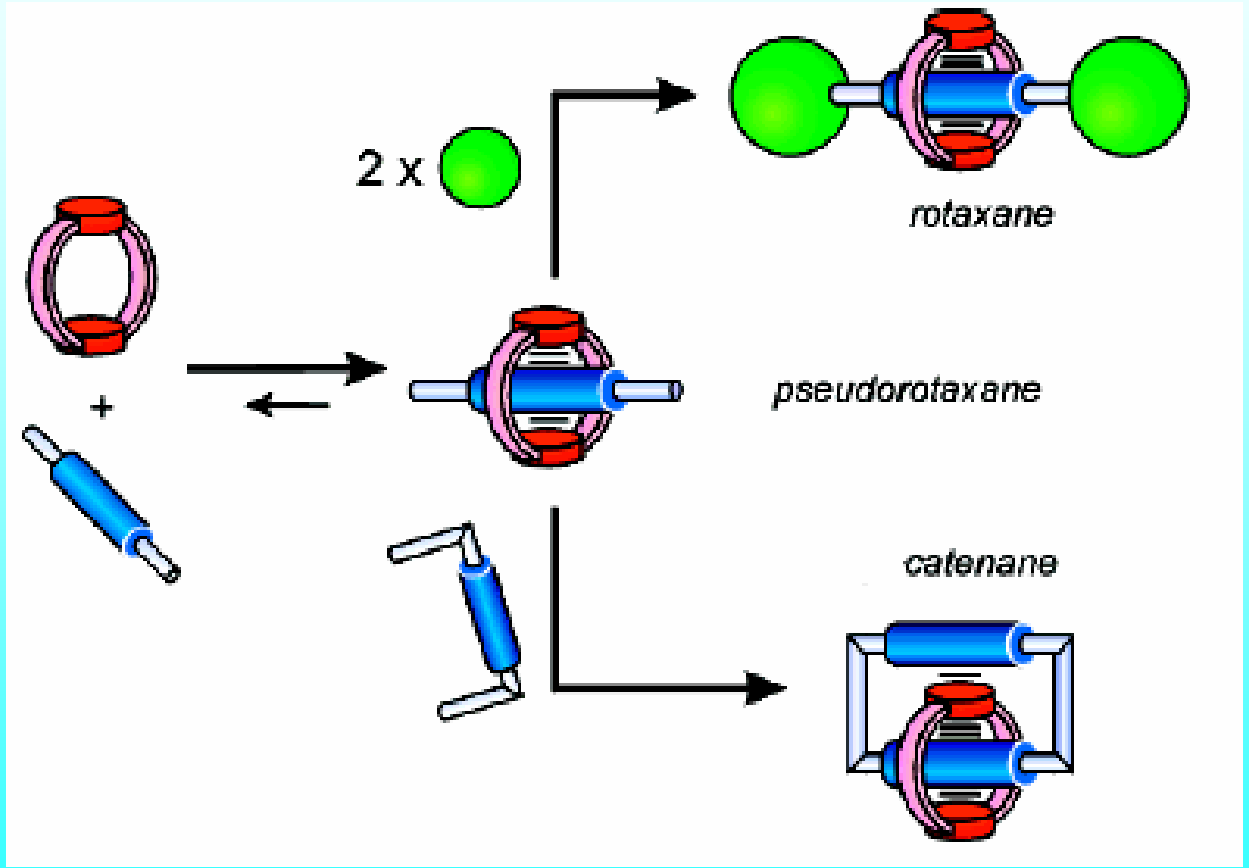
Main trends in molecular machines design are concerned with rotaxanes and catenanes



R. Ballardini et al.
Angew. Chem. Int. Ed. 2000, 39, No. 19

A rotaxane pH controlled molecular switch

The Cycle Proceeds as Follows:

1. Crown on the Ammonium 'Station'

The protonated amine binds the crown ether more strongly than the bipyridinium. This complex is colorless.

2. Addition of Base

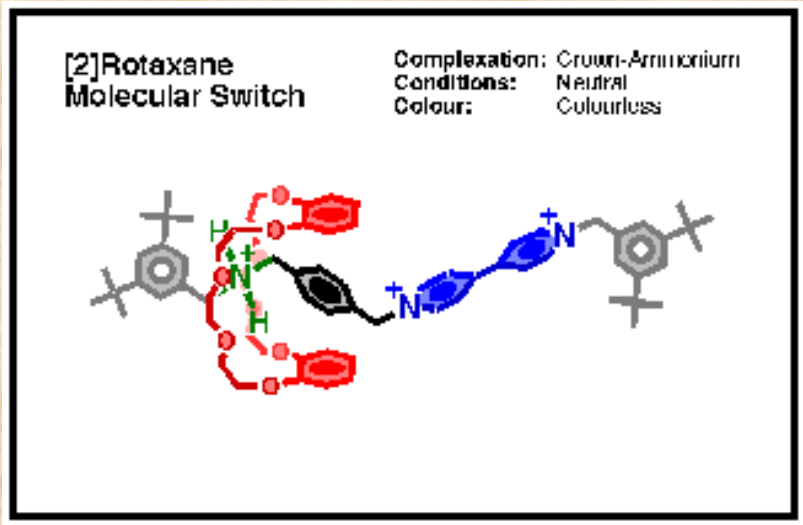
After deprotonation by diisopropylethylamine, the ammonium 'station' has become a free amine, incapable of binding the crown ether. The strongest binding site is now the bipyridinium 'station', so the crown ether moves towards it. π-π stacking interactions between the bipyridinium and the aromatic units on the crown ether cause the solution to become an orange color.

3. Crown on the Bipyridinium 'Station'

While the bipyridinium 'station' is the only binding site, the crown ether resides upon it.

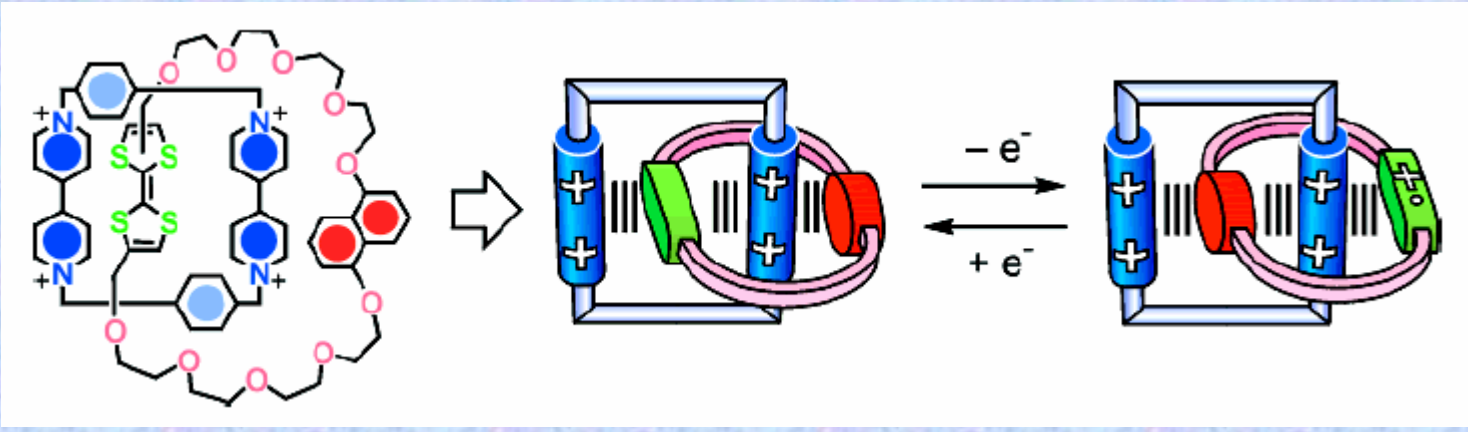
4. Addition of Acid

The addition of trifluoroacetic acid protonates the amine, giving rise to an ammonium center. This 'station' is capable of stronger complexation of the crown ether than is the bipyridinium, and so the crown ether moves back to it, causing a loss of the orange color.



By JFS Group, Univ. of California, LA

In our work we touched upon functioning of the catenane – compound with two interlocked molecular rings. This catenane is known for the rotary movements of one of its rings occuring upon oxidation/reduction.



R. Ballardini et al.
Angew. Chem. Int. Ed. 2000, 39, No. 19

A [2]catenane-based solid state electronically reconfigurable switch

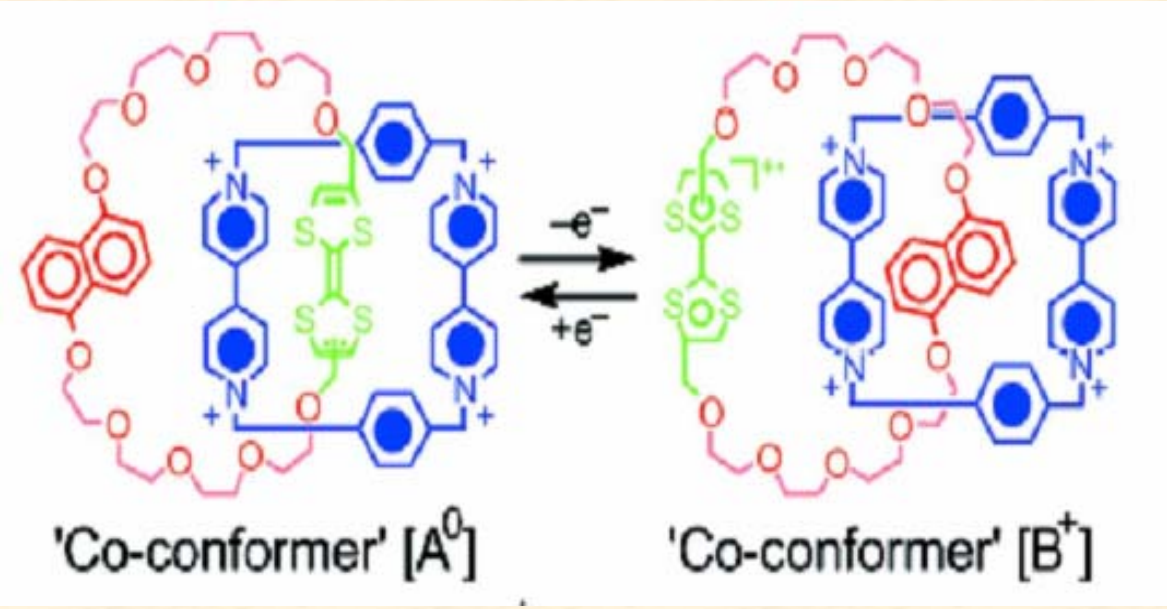


Figure from
Charles P. Collier et al.,
Science, 289 (2000)
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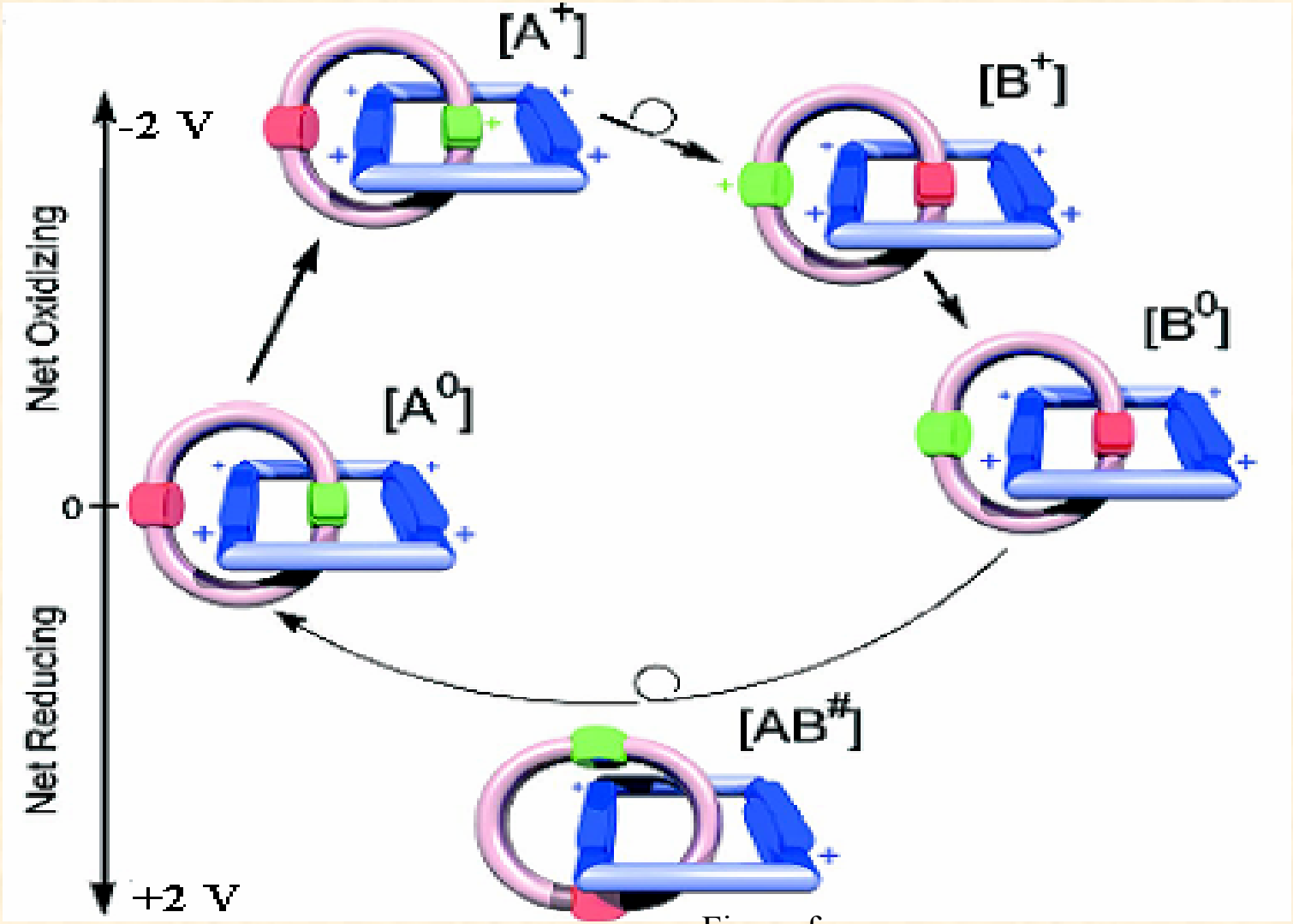

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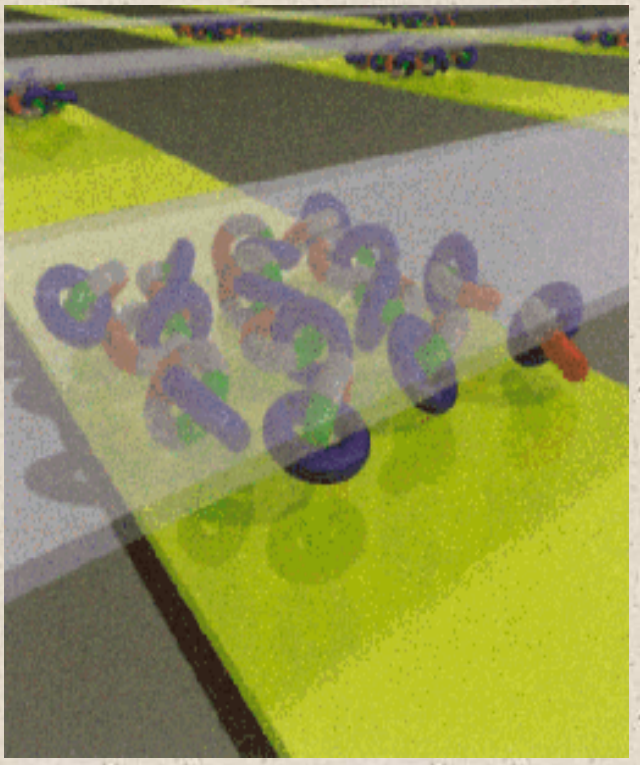

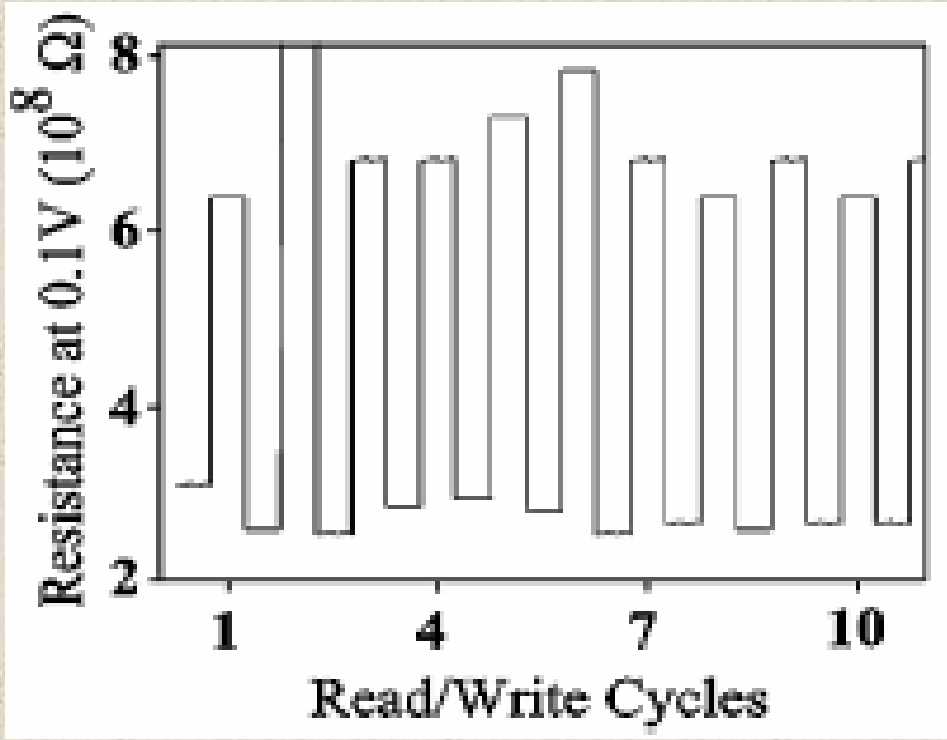

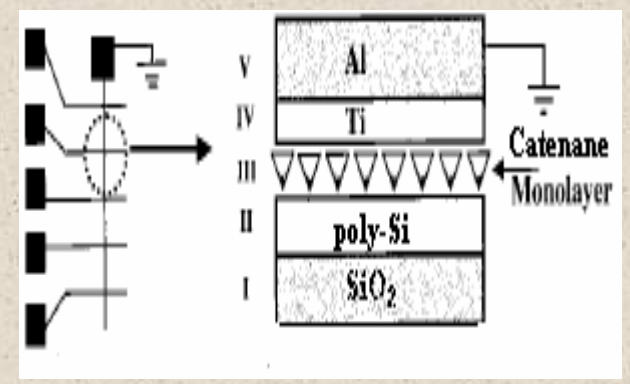

Scheme of the catenane device

Charles P. Collier et al.,
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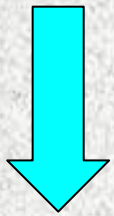
So, there is a molecule with known electroconductive properties which depend on its conformation, but dynamics of conformational transitions is not obvious, there is only electrochemical data and data of absorption optical spectroscopy.



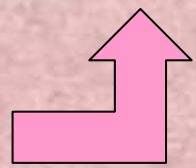
Investigation methods *in silico (computer-simulated)* help to study dynamic correlations in systems of such size in detail.

1st stage of the research

Three cationic forms of the catenane (A^0, B^+ and $AB^{\#}$) were subjected to geometrical optimization. Initial structure of the catenane was taken from Cambridge Crystallographic Data Centre (CCDC)

Then the three structures were subject to quantum chemical calculation of molecular charge distribution.

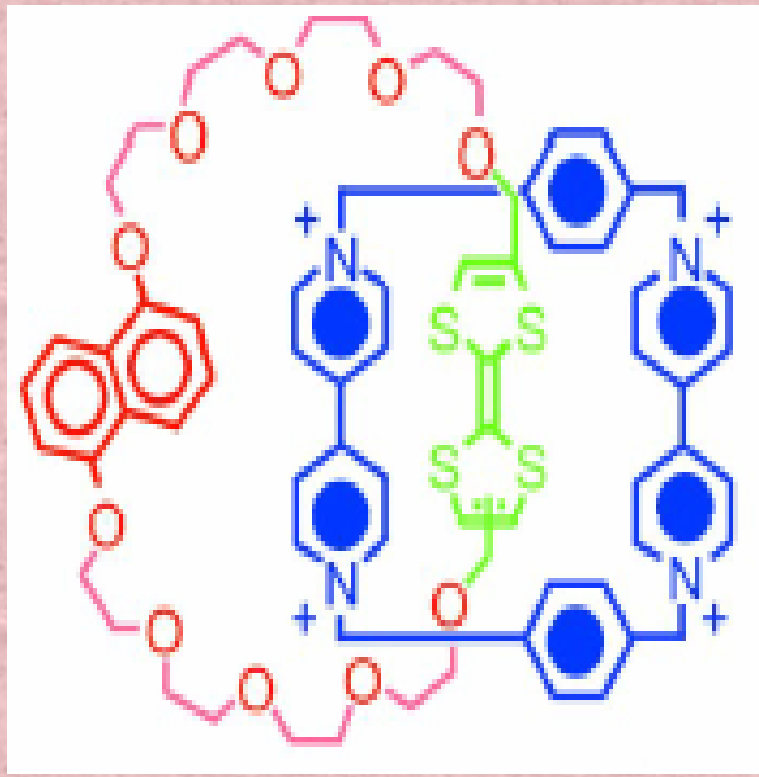
Restricted Hartree-Fock method with open shells was used, and the optimization was carried in STO-3G basis with descent in one of the quasi-Newton-Raphson method varieties. The partial charges were calculated according to Loewdin.



The whole quantum chemical set of calculations was executed in software package GAMESS©

1st stage of the research (continue)

Quantum chemical calculations confirmed considerations concerning constituent functional groups participation in redox processes. The considerations were known before from organic chemistry. π-electron acceptor status of the charged cyclophane ring bipyridine nitrogens and π-electron donor status of the tetrathiafulvalene ring nonoxidized sulfur are seen in such system.



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1st stage of the research (continue)

Comparative analysis of existing atom types of Amber99© force field, used in calculation of classical molecular dynamics, became the final part of the first stage of the research. Taking into account the geometry of the structures optimized to some extent, new types of atoms, bonds, valent and torsion angles were assigned. Charges were assigned according to the previous quantum chemical calculations.

Partial charges of the atom types used

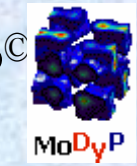
In case of types corresponding to different by chemical surroundings atoms the mean charge is given (atoms were ascribed the same charge only if they convert to identical by chemical surroundings atoms when being reflected relative to symmetry plane).

Name of a chemical residuum		Atom type	A^0	B^+	$AB^\#$
cyclophane ring	tetrathiafulvalene part	S	+0,024	+0,194	+0,037
		CD	-0,103	-0,040	-0,089
		CW	-0,013	-0,002	-0,022
		CV	-0,076	-0,060	-0,092
	naphthalene part	CX	-0,057	-0,066	-0,067
		CE	+0,031	+0,019	+0,025
		CB	-0,013	-0,011	0,012
	crown-ether bridges	OS	-0,161 – -0,216	-0,166 – -0,198	-0,158 – -0,193
tetrathiaful-valene ring	bipyridine part	N	+0,024	+0,017	-0,064
		CM	+0,038	+0,049	+0,018
		CD	+0,090	+0,091	+0,040

2nd stage of the research

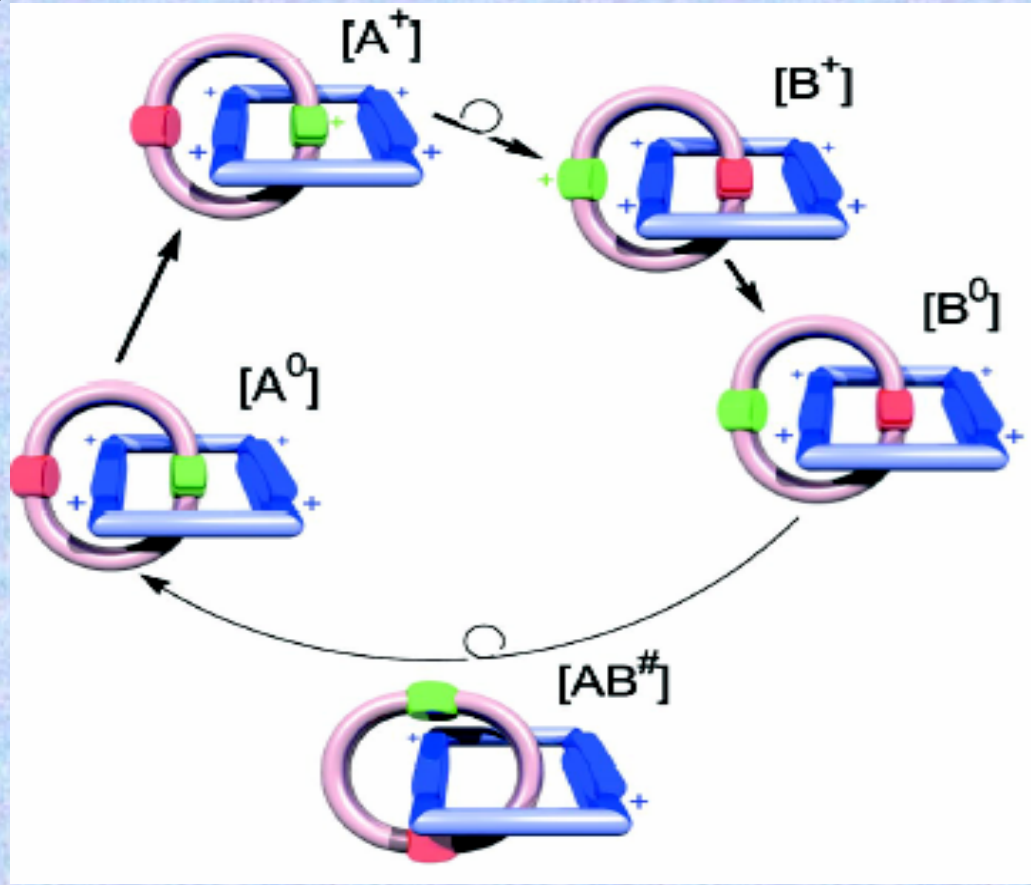
The following stage of the work was an investigation of the catenane at the level of molecular mechanical approximation. Present work was a kind of methodical one, it was essential to learn how to estimate such mutually rotating systems.

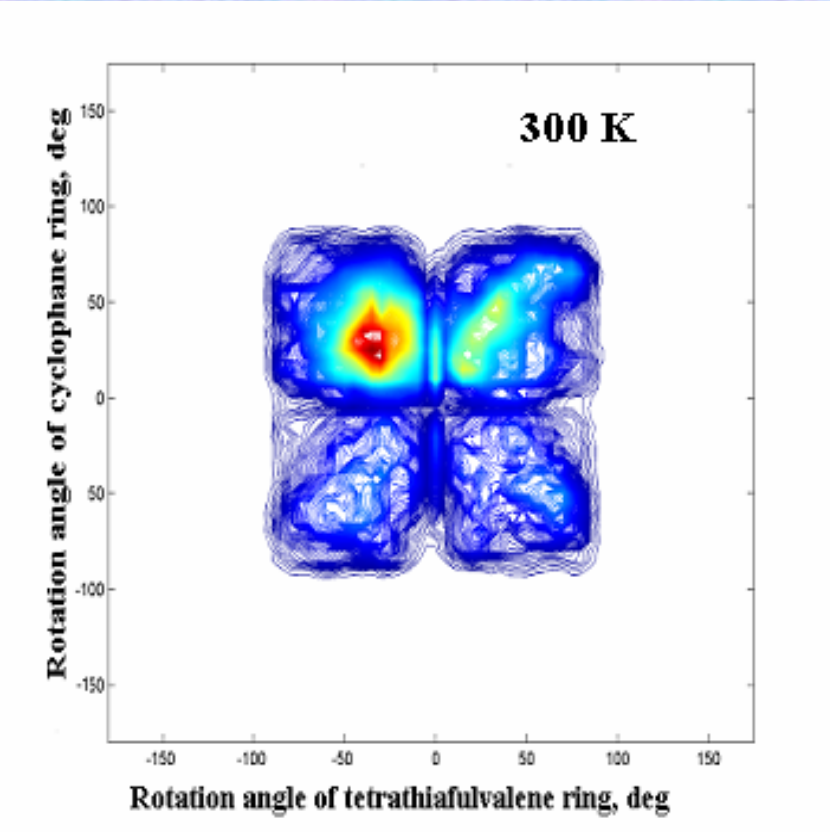
The calculation was carried out in package MoDyP© (http://www.moldyn.ru/modyp)

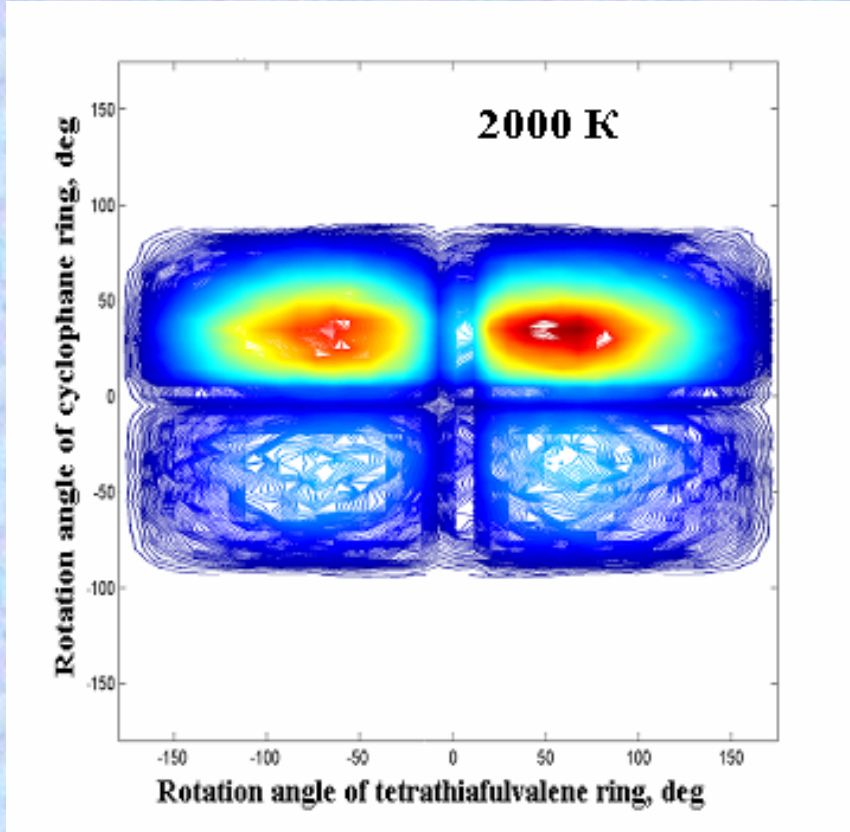


Molecular dynamics was conducted for one chosen molecule of the catenane under different conditions, common of which were a step of integration - 0.001 ps, - combined use of NVT and collision thermostats (average frequency of collisions with virtual particles was 100 per ps per atom, weight of the particles was 18 a.w.u.), and also radiuses of truncating for Coulomb and Van-der-Waals interactions - 15 A and 12 A, accordingly. Temperature varied from 300 K to 2000 K. The range of trajectories length was from 10 ns to 1 μs.

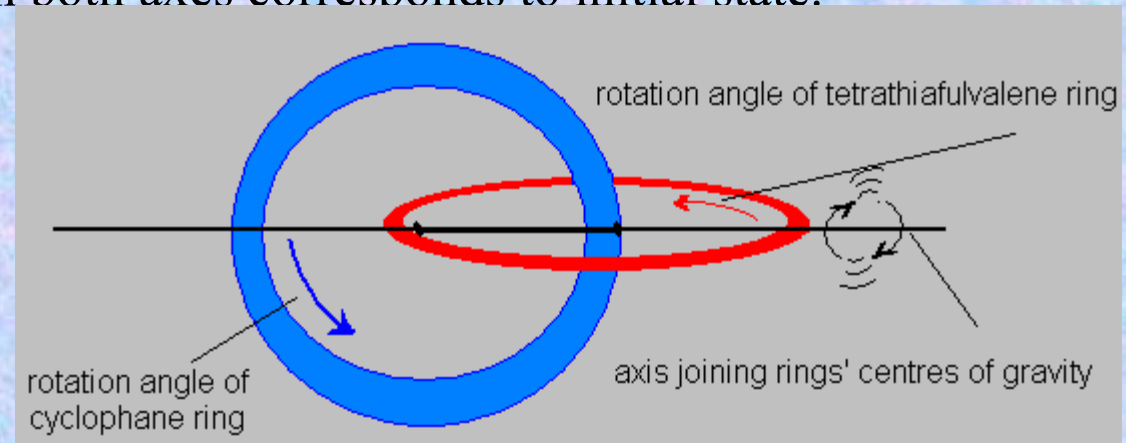
So, the results

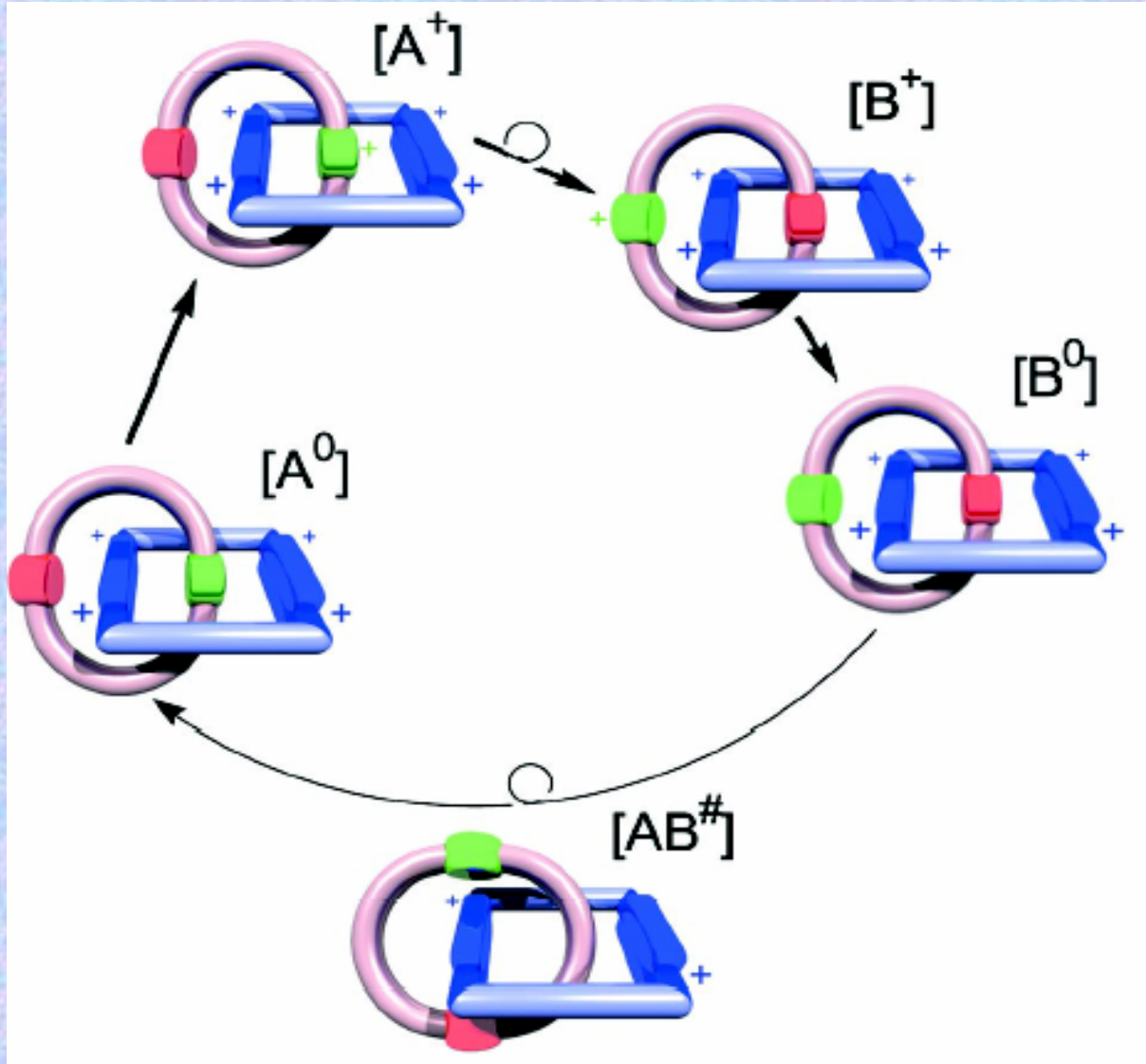


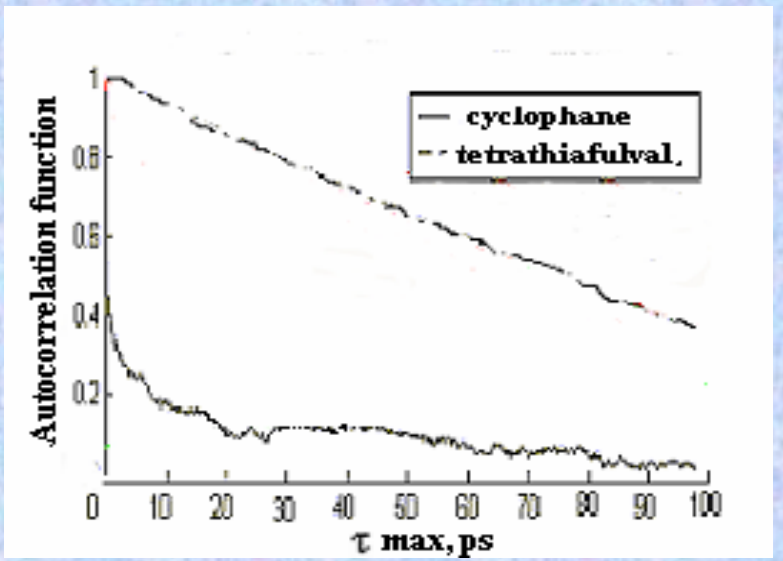


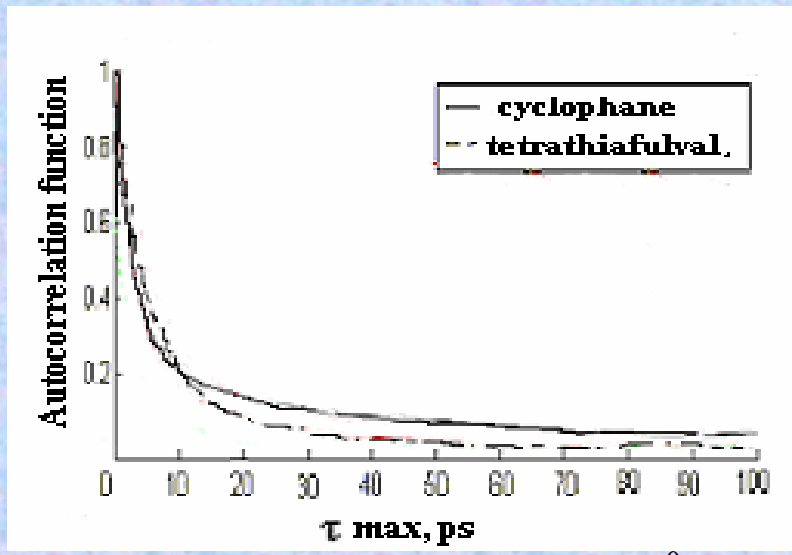


Density of states of rotation angles of the rings in [A^0] co-conformer. Zero on both axes corresponds to initial state.




[A+]
[B+]
[B0]
[A0]
[AB#]

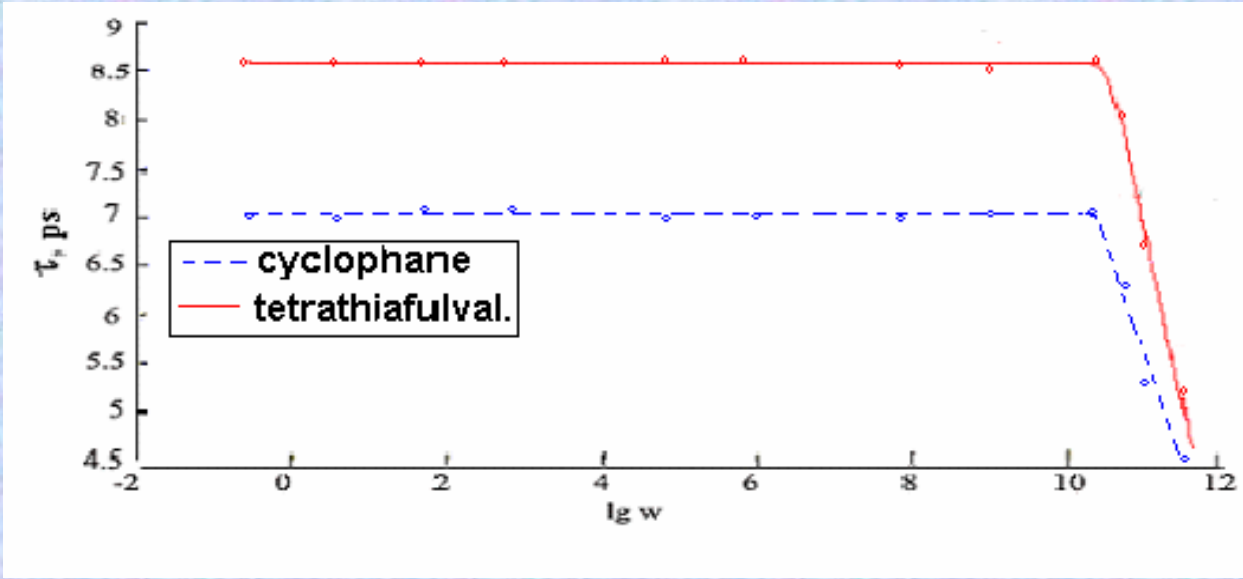




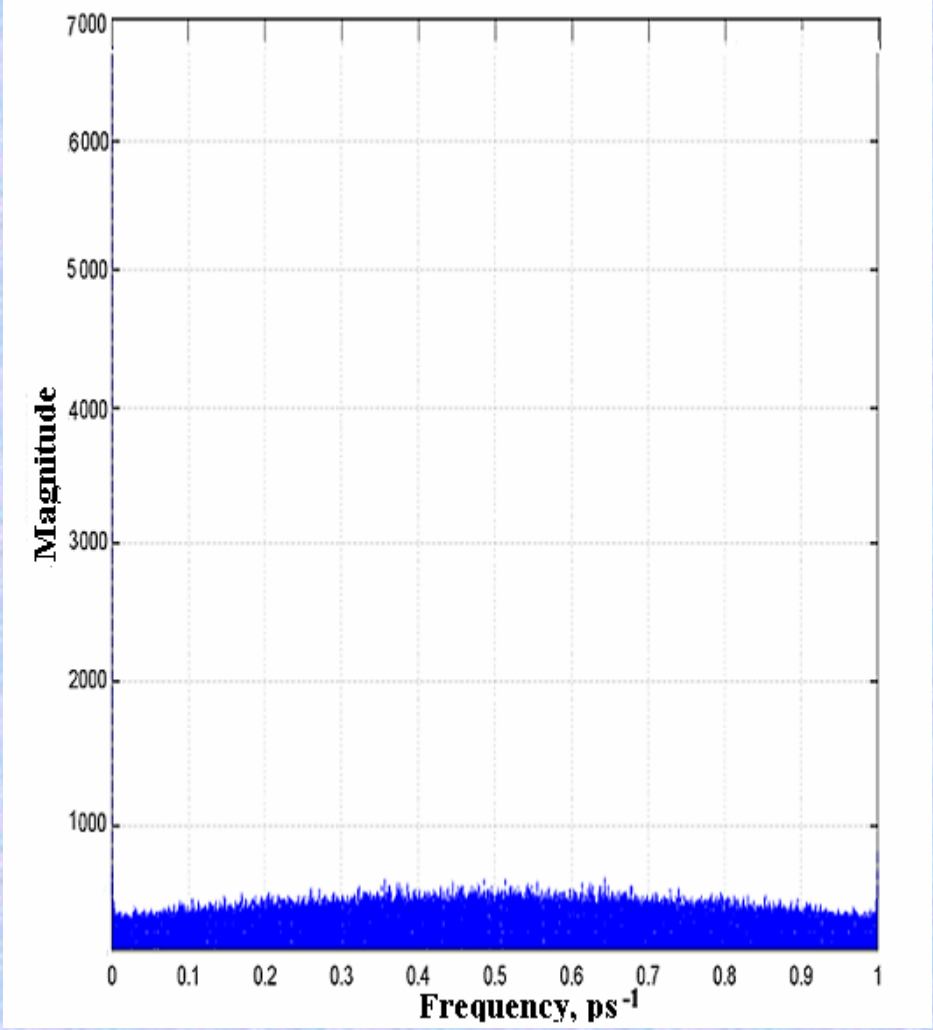
Comparison of autocorrelation functions of dipole moments for the catenane [A^0] system with fixed cyclophane ring (on the left) and fixed tetrathiafulvalene ring (on the right). Temperature 300 K. The dipole moments were calculated relative to the centre of gravity for the whole catenane:

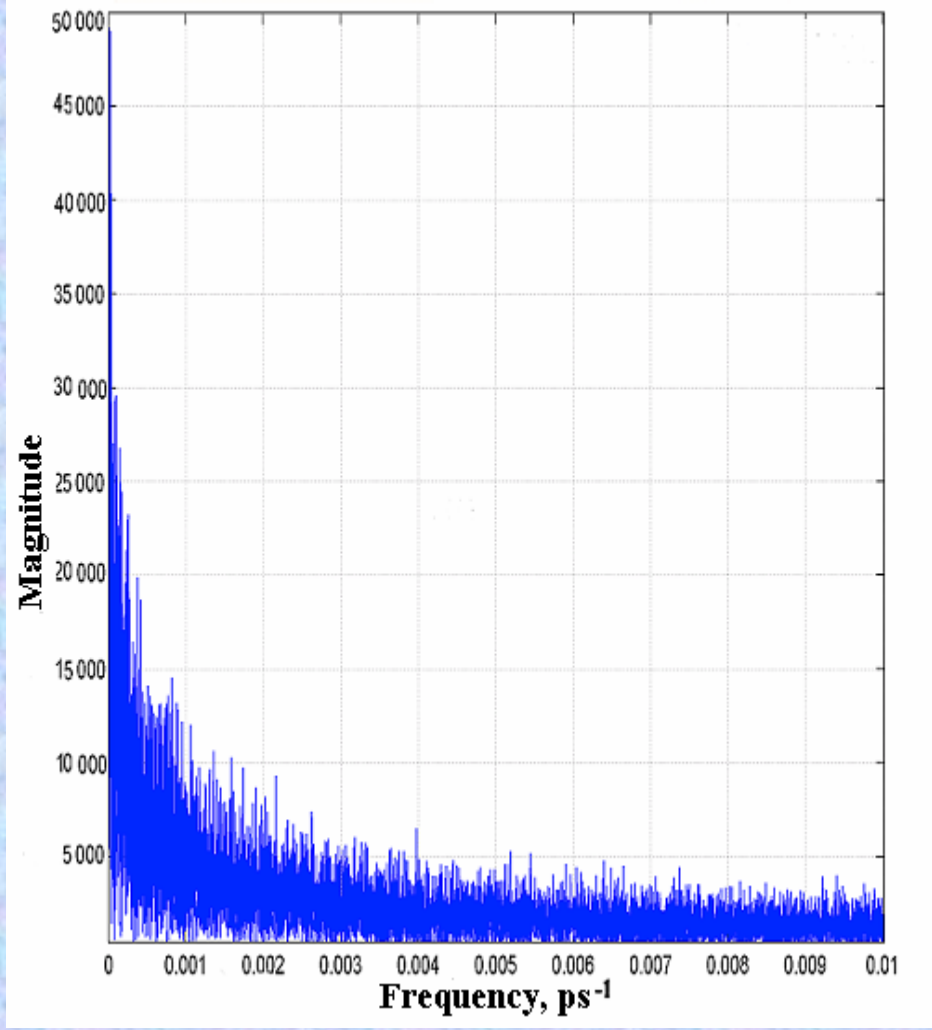
$$\overrightarrow{p} = \sum_{i=1}^{n} q_i \cdot (\overrightarrow{r_i} - \overrightarrow{R_m}),$$

where q_i denotes charge of i^{th} atom in a ring, $\overrightarrow{r_i}$ – its radius-vector, $\overrightarrow{R_m}$ – radius-vector of the centre of gravity for the whole molecule.

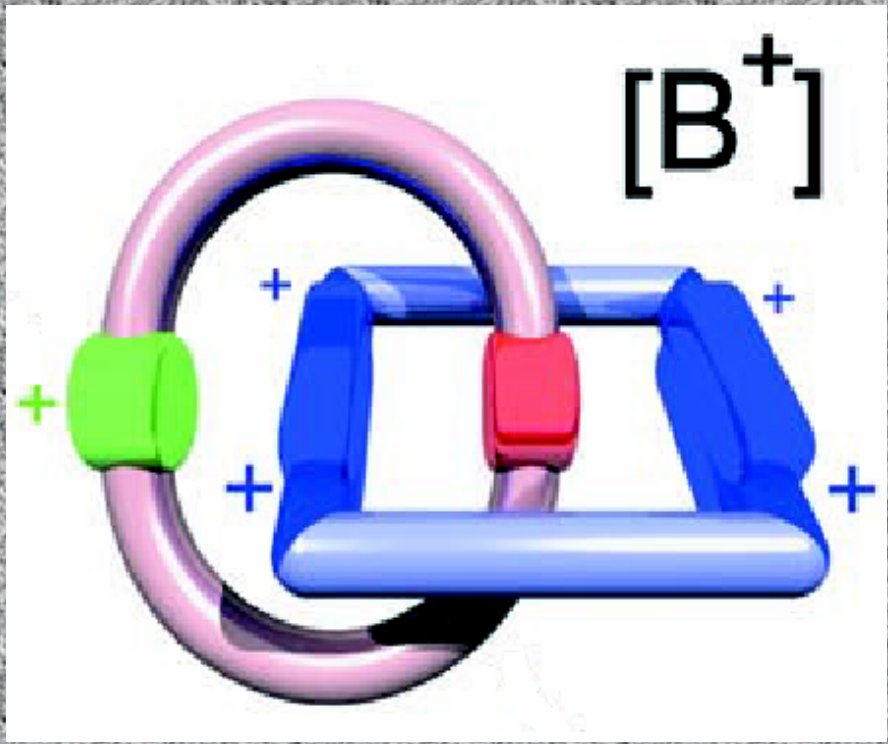


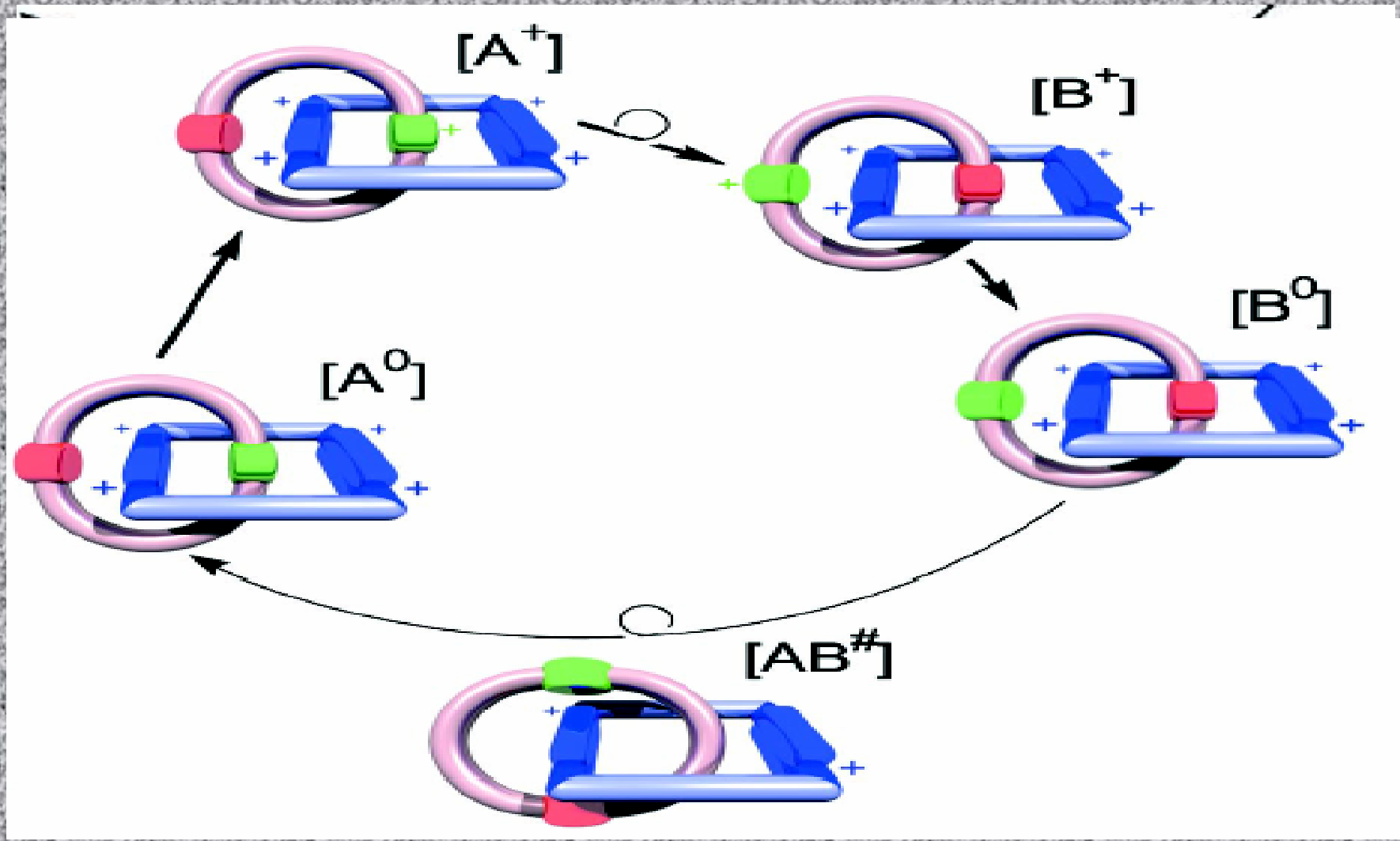
Dependence of autocorrelation time τ of dipole moments of both of rings on frequency w of imposed electric field. Electric intensity amounts to $7.2 \cdot 10^6$ V/cm. It corresponds to the intensity of point charge $2e^-$ at a distance of 20 A in vacuum (20 A is a characteristic size of the catenane; the catenane could be placed into a cube with edges of such size). The field was directed along the axis joining rings' centres of gravity in the initial structure.





Fourier expansions of angular rotation velocities of the rings in catenane [A^0] at 300 K. At the left – cyclophane ring, at the right – tetrathiafulvalene ring.


[B+]


[A+]
[B+]
[BO]
[AO]
[AB#]

At last, conclusions

Movements of constituent rings in [A^0] (i.e. initial) co-conformer

large-scale rotation of tetrathiafulvalene ring with angle more than 180º

rapid stochastic rotary movements of both rings

Movements of constituent rings in [B^+] and [$AB^\#$] co-conformers

the rings don't rotate greatly during 100 ns calculation even at 2000 K; fast stochastic movements occur

Thank you for your attention


THE LORD OF THE RINGS
THE TWO TOWERS
Watch the movie on Xmas Eve