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Molecular mechanics (MM3(π)) conformational analysis of molecules containing conjugated π-electron fragments: a molecular tweezer

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Dedicated to Academician Ivan Juchnovski on the occasion of his 70th birthday

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The conformations of a molecular tweezer formed by two aromatic chiral molecules, bonded and separated, by a conjugated spacer, were studied with molecular mechanics. This molecule contains conjugated π-electron fragment and necessitates special treatment with the MM3(π) modeling protocol. Comparison was made with results from the standard MM3 scheme and semiempirical and *ab initio* MO, and DFT quantum-mechanical methods. The CONFLEX conformational search procedure was used for finding low-energy conformations. Although one and the same cluster of conformations for the molecular tweezer is strongly preferred when using the two molecular mechanics modeling protocols (MM3 and MM3(π)), differences were obtained in the geometries of the lowest-energy conformations.

Key words: molecular tweezer, conformational analysis, molecular mechanics, MM3(π), CONFLEX search.

INTRODUCTION

We reported recently results from molecular mechanics study of the preferred conformations of tylosin [1, 2] and leucomycin-V [3]. We emphasized in these studies the dependency of the results on the molecular mechanics protocol used and the completeness of the conformational search. A thorough search for the lowest energy conformations based on the CONFLEX [4–6] procedure as a searcher and the MM3(92) force field [7–10] as a molecular mechanics model was performed. Two problems are of particular importance when molecular mechanics is used for modeling the conformations of large molecules: (i) the proper choice of a force field for modeling the system under study; (ii) reliable and efficient conformational search of low-energy conformations when many degrees of freedom for intramolecular rotations determine the conformational flexibility of the molecule. A specific characteristic and an advantage of the Allinger's MM3 force field is that an extension of the force field, MM3(π) [11, 12], has been devised to model molecules with conjugated π-electron fragments.

As an overall result of methodological signifycance from an earlier study [3] is the differences that manifest two very similar molecules, leucomycin-V and its 9-epi isomer (they differ only by the chirality of the C(9) macroring carbon atom), when comparative studies are carried out using the MM3 and MM3(π) molecular mechanics modeling protocols. This prompted us to extend further our study by examining also the conformations of a molecular tweezer containing conjugated π-electron spacer – di-(R,R)-1-[10-(1-hydroxy-2,2,2-trifluoroethyl)-9-anthryl]-2,2,2-trifluoroethyl muconate (**1**). A cautionary note is made in the present report regarding the execution of conformational search/minimization studies in the case of cooperative movements of the atoms on potential energy surface of small slope – molecules like **1**, where aromatic rings are present [13].

The chiral molecular tweezer (**1**) (Fig. 1) was synthesized recently. It contains conjugated π-electron spacer and behaves as an excellent chiral solvating agent (CSA) [14]. CSA are optically pure compounds that after binding pairs of enantiomers produce diastereomeric associates with different NMR spectra. Common CSAs can usually participate in hydrogen bonds or π interactions. Some non-cyclic compounds with flexibly-sized cavities, which are frequently termed molecular tweezers or clips, proved to be effective as synthetic receptors. This kind of compounds is characterized by having two planar aromatic groups, separated by a semi-rigid spacer, which enhances the selective binding with aromatic guests by π interactions [15]. Molecular tweezers are studied also in relation to elucidating the mechanisms of the recognition of

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sequence information in high-molar mass copolymers by small molecules of complementary structure [16]. Intensive research is carried out on such systems during the last two decades [17–50].

Dihedral angle	
D_1	1-2-3-4
D_2	1'-2'-3'-4'
D_3	2-3-4-5
D_4	2'-3'-4'-5'
D_5	3-4-5-6
D_6	3'-4'-5'-6'
D_7	4-5-6-7
D_8	4'-5'-6'-7'
D_9	8-9-10-11
D_{10}	8'-9'-10'-11'
D_{11}	9-10-11-12
D_{12}	9'-10'-11'-12'
D_{13}	2-1-1'-2'

Fig.1. Numbering of the atoms in di-(R,R)-1-[10-(1-hydroxy-2,2,2-trifluoroethyl)-9-anthryl]-2,2,2-trifluoroethyl muconate (**1**) and the definition of dihedral angles.

METHOD AND COMPUTATIONAL DETAILS

The version 3.6 of CONFLEX [4–6] was used. A gradual increase to a search limit of 4.0 kcal·mol^{-1} for **1** determined the energy range from which the initial structures for the search were selected [4-6]. The variable torsional angles (Fig. 1), which were used for conformation comparison when eliminating identical conformers are: D1 = 1 – 2 – 3 – 4, D2 = 1' – 2' – 3' – 4', D3 = 2 – 3 – 4 – 5, D4 = 2' – 3' – 4' – 5', D5 = 3 – 4 – 5 – 6, D6 = 3' – 4' – 5' – 6', D7 = 4 – 5 – 6 – 7, D8 = 4' – 5' – 6' – 7', D9 = 8 – 9 – 10 – 11, D10 = 8' – 9' – 10' – 11', D11 = 9 – 10 – 11 – 12', D12 = 9' – 10' – 11' – 12', D13 = 2 – 1 – 1' – 2'. Nine dihedrals describe the geometry of the π-conjugated bridge and these are the angles which were used for cluster analysis in Table 1 [because of the preferred s-trans conformation for this fragment of the π-spacer, D13 is always about 180° degrees, a letter-code ***A*** (*vide infra*)]. The default values of the options were used when the steric energies and the dihedral angles were compared in the redundancy test, e.g. 3N/100 kcal·mol^{-1} (N – the number of atoms) allowance for the comparison of steric energies in the first stage, and 10.0° allowance for the comparison of dihedral angles in the final stage. The whole set of conformations were subjected to a cluster analysis [51, 52] and the structures resulted sorted into 2 clusters (Table 1). Unique conformations were processed with the π-version of the MM3(92) program [10–12]. This approach is more economical than the direct search with the computational scheme for modeling conjugated π-electron segments in the molecule. In addition, an independent CONFLEX/MM3(π) search/minimization study was also executed. The block-diagonal Newton-Raphson minimization procedure was used [10]. Electrostatic interactions were estimated with the value 2.0 of the dielectric parameter.

RESULTS AND DISCUSSION

Computed conformational data for 1 are summarized in Table 1. They include average steric energies and populations of clusters and a letter-code representation of the important dihedral angles (Table 1). For the sake of compactness of the presentation we used a letter-code designations of dihedral angles as given in Fig. 2 [1]. Letter ***G*** designates a dihedral angle in the range from 20 to 100°, $\underline{\boldsymbol{G}}$ - from 100 to 150°, ***A*** - from 150° to –150°, *etc.*

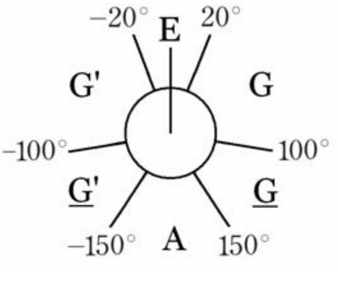


Fig. 2. Designation of dihedral angles.

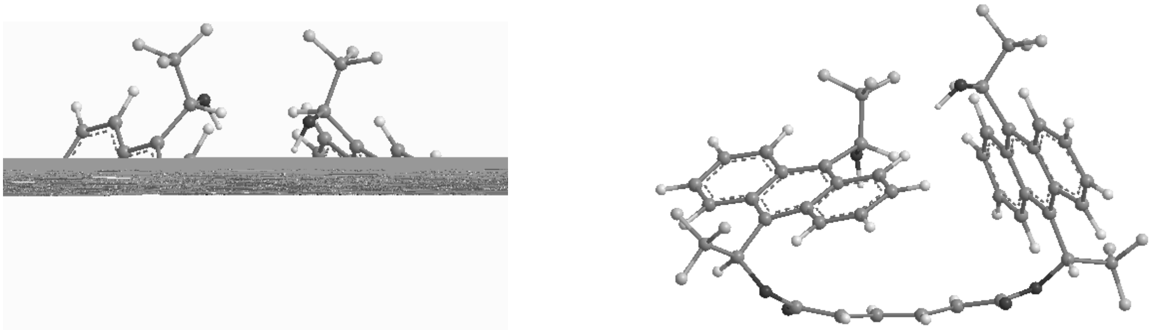
Table 1. Cluster analysis of low-energy conformations of di-(R,R)-1-[10-(1-hydroxy-2,2,2-trifluoroethyl)-9-anthryl]-2,2,2-trifluoroethyl muconate (**1**) [a].

Clusters	Dihedral angles								Number of conformations	ΔE_0 [b]		ΔEav [c]	Population [d]
	D1	D2	D3	D4	D5	D6	D7	D8		MM3	MM3(π)		
I	A	A	G	G	G’	G’	G	G	460	0.0	0.0	0.9	0.990
II	A	E	A	A	G’	G’	G	G	85	3.6	4.0	4.4	0.010

a - Units are kcal·mol^{-1}; b - Relative steric energy of the lowest-energy conformation of the cluster. CONFLEX search has been carried out with the MM3 protocol. Search limit 4.0 kcal·mol^{-1} was used. The final set of coordinates for the lowest-energy conformations of each cluster was subjected to MM3(π) minimization. The independent CONFLEX/MM3(π) was executed with search limit 1.5 kcal·mol^{-1}; c - Average steric energy of the cluster; d - At 300K.

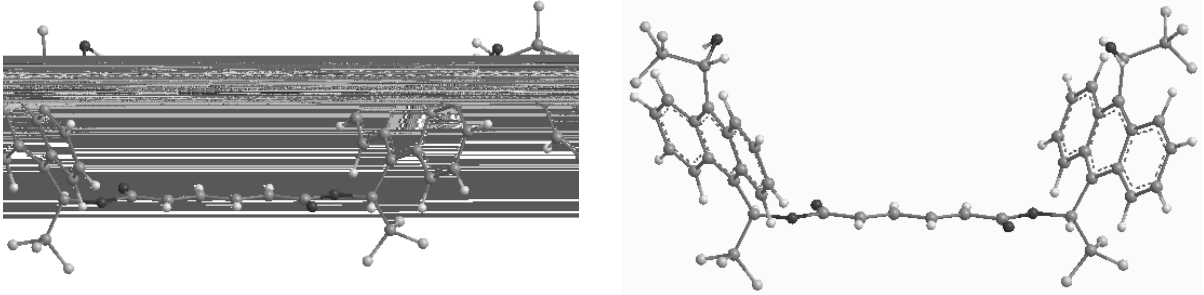
We have emphasized in our previous work [2, 3] the importance of using at the final stage of the minimization the version of MM3 devised to model molecules with conjugated π-electron fragments. Such a kind of treatment required the dienone portion of tylosin [2] and the diene fragment of leucomycin-V [3]. The overall result from the present study on **1** is that the conjugated π-electron spacer of the molecular tweezer **1** necessitates MM3(π) treatment. The concavely arranged host geometry of the two anthracene rings bound with the chiral $CHOHCF_3$ groups is important for the selective binding with aromatic or other guests. The conformational equilibrium and the C2 symmetry of **1** make it impossible to study its global geometry using NMR experiments [14]. Molecular mechanics modeling is of particular usefulness in such situations. Although one and the same cluster of conformations is strongly preferred when using the two molecular mechanics modeling protocols (CONFLEX/MM3 and CONFLEX/MM3(π)), significant differences of the geometries for the π-bridge portion were obtained in the lowest-energy conformations (Fig. 3, A, B and Table 2, data in ‘bold’). These differences in the geometries did not appear however when using CONFLEX/MM3 search with subsequent MM3(π) minimization (Tables 1 and 2). We had to carry out an independent CONFLEX/MM3(π) search/minimization study (Fig. 3, B). This is purely “technical” artifact that originates from the block-diagonal Newton-Raphson minimization procedure in MM3 that may not always produce completely converged results for molecules containing aromatic rings, as they present cases with cooperative movements of the atoms on a surface of small slope [13].

Attempting further to interpret the results, we compared the geometries derived with molecular mechanics with semiempirical molecular orbital (SE-MO) [53–55] and *ab initio* MO (RHF/6-31G*), ant DFT (hybrid functionals B3LYP and MPW1K with basis set 6-31G*) [56] methods (Table 2). The CONFLEX/MM3 and CONFLEX/MM3(π) optimized geometries of the lowest-energy conformations (Fig. 3, A and B) served as starting structures for the AM1, PM3, and Hartree-Fock computations. The ab initio MO optimized structure was used as starting geometry for the DFT calculations. Gaussian 98 was used for all quantum-mechanical computations [56]. Significantly different final geometries were obtained (Fig. 3). The spacer of the muconate (**1**) connecting the two chiral arms is now flatter compared with the geometries from the molecular mechanics modeling, i.e. the tweezer does not possess enough flexibility and the two arms of the clip are positioned more distant from each other (Fig. 3, C–H). This result is not unexpected because the SE-MO, HF *ab initio* MO and standard DFT methods cannot model enough satisfactorily dispersion interactions and the system lacks forces that could deform the linear spacer. Structures C and D (AM1) have the same geometry of the conjugated spacer, but differ by the rotation of the $CHOHCF_3$ groups. Similar is the geometry of E, whereas the geometry of F (PM3) is completely different in comparison with all low-energy forms obtained after the CONFLEX search. Quite probably, the *syn* disposition of the anthracene rings in this case does not correspond to a local minimum on the PM3 potential energy surface. The present case, muconate **1**, illustrates the different behaviour of the two SE-MO methods (cases D and F), as well as the importance of proper choice of the starting geometry (cases A and B). Except for PM3, all other quantum-mechanical methods produce symmetrical geometries (Table 2). The DFT optimized clips are more opened compared with the structures obtained with the other modeling protocols (compare G and H on Fig. 3 and the torsion angles D5, D6 in Table 2). It is gratifying, however, that in the prevailing number of cases cavities are produced after the optimizations with the SE-MO, *ab initio* MO and DFT methods (cases C, D, E, G, and H).



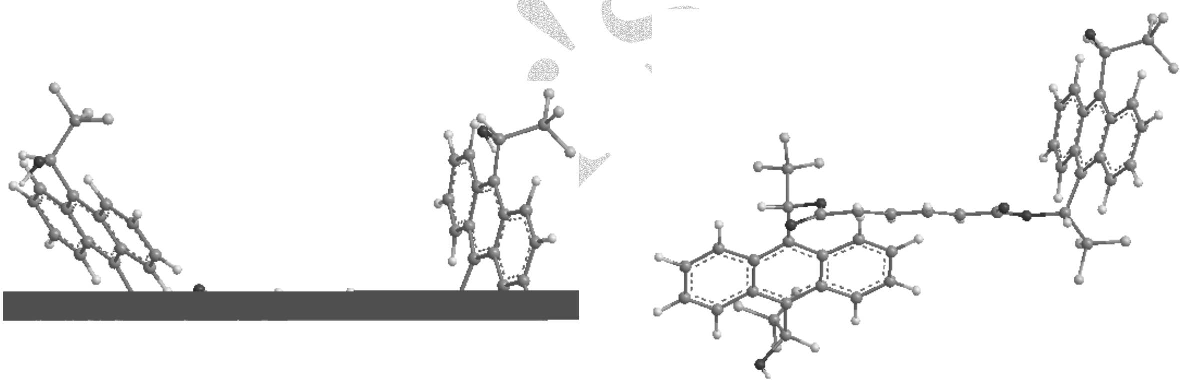
A CONFLEX/MM3

B CONFLEX/MM3(π)



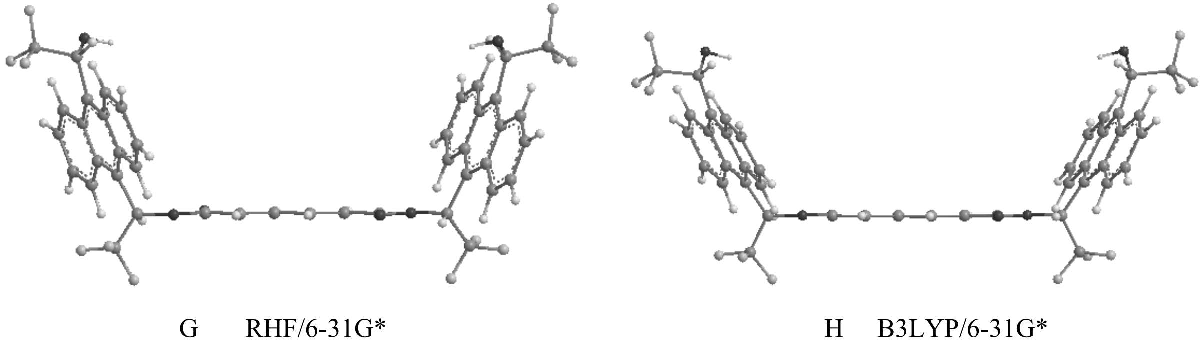
C AM1 (1.4)
(after CONFLEX/MM3)

D AM1 (0.0)
(after CONFLEX/MM3(π))



E PM3 (0.0)
(after CONFLEX/MM3)

F PM3 (0.4)
(after CONFLEX/MM3(π))



G RHF/6-31G*
(after CONFLEX/MM3)

H B3LYP/6-31G*
(after RHF/6-31G*)

Fig. 3. Optimized geometries of the lowest-energy conformations of **1**. Relative AM1 and PM3 energies (in kcal·mol^{-1}) are given in parentheses.

Table 2. Comparison of the geometries (dihedral angles in degrees) of the lowest-energy conformations of **1** obtained with different methods.

Method	D1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11	D12	D13
A [a] - CONFLEX/MM3 [b]	–174.6	–174.9	142.1	143.1	–62.1	–62.9	136.4	136.6	138.1	137.9	–61.9	–61.0	–175.0
B - CONFLEX/MM3(π) [c]	–153.9	–174.6	138.1	144.3	–54.2	–76.3	138.9	136.3	141.1	137.9	–62.8	–69.1	–167.7
MM3(π) [d]	–170.4	–172.0	141.0	142.2	–63.8	–65.1	136.6	136.8	138.1	137.9	–62.6	–61.3	–174.0
C - AM1 [e]	179.1	179.1	179.9	179.9	–114.1	–114.1	143.9	143.9	143.0	143.0	–25.0	–25.0	179.7
D - AM1 [f]	179.9	179.9	179.2	179.2	–115.3	–115.3	144.4	144.3	127.5	127.5	49.4	49.4	–179.8
E - PM3 [g]	177.7	–179.7	178.2	178.2	–110.7	–94.6	145.0	133.1	144.8	127.8	–62.8	55.9	–179.3
F - PM3 [h]	–27.6	–179.2	175.9	178.2	–100.2	–94.2	145.9	133.1	143.9	127.8	–64.5	56.0	179.3
G - RHF/6-31G* [i]	179.5	179.5	180.0	180.0	–103.5	–103.6	139.4	139.4	140.1	140.1	–52.3	–52.3	179.8
RHF/6-31G* [j]	179.4	179.4	180.0	108.0	–103.7	–104.3	139.4	139.3	140.1	140.1	–52.2	–52.3	179.8
H - B3LYP/ 6-31G* [k]	–179.5	–179.5	–179.2	–179.2	–119.0	–119.0	138.7	138.7	140.0	140.0	–40.0	–40.0	–179.5
MPW1K/6-31G* [l]	–179.7	–179.7	–179.5	–179.5	–118.8	–118.8	138.3	138.3	139.7	139.7	–35.2	–35.2	–179.5

a - The structures A-H are given in Fig. 3; b - CONFLEX/MM3 search; c - CONFLEX/MM3(π) search; d - MM3(π) optimization after CONFLEX/MM3 search. The lowest-energy structure obtained in this way practically preserves its starting geometry (A) and it is not given on Fig. 3; e - AM1 optimized geometry after CONFLEX/MM3 search; f - AM1 optimized geometry after CONFLEX/MM3(π) search; g - PM3 optimized geometry after CONFLEX/MM3 search; h - PM3 optimized geometry after CONFLEX/MM3(π) search; i - RHF/6-31G* optimized geometry after CONFLEX/MM3 search; j - RHF/6-31G* optimized geometry after CONFLEX/MM3(π) search. HF optimized examples show identical geometries (energies) and only one structure is given in Fig. 3; k - B3LYP/ 6-31G* optimized geometry after RHF/6-31G*; l - MPW1K/6-31G* optimized geometry after RHF/6-31G*. Both DFT optimized structures are with the same geometries.

The lowest-energy MM3(π) structure of cluster II (Table 1) was also optimized with the SE-MO, and *ab initio* MO and DFT methods. The geometries obtained resemble structure F in Fig. 3. The *anti* disposition of the chiral clips (cluster II) is disfavoured energetically by about 1–2 kcal·mol^{-1} in all cases.

CONCLUSIONS

Although one and the same cluster of conformations of **1** is strongly preferred when using the two molecular mechanics modeling protocols, significant differences were obtained in the geometries of the lowest energy conformations (Fig. 3, A and B). Both the molecular mechanics and quantum-mechanical methods confirm the prevalence of conformation that can easily adapt to a small molecule substrate by formation of a chiral cavity [14].

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МОЛЕКУЛНО-МЕХАНИЧЕН (MM3(π)) КОНФОРМАЦИОНЕН АНАЛИЗ НА МОЛЕКУЛИ СЪДЪРЖАЩИ СПРЕГНАТИ π-ЕЛЕКТРОННИ ФРАГМЕНТИ: МОЛЕКУЛНА ПИНСЕТА

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(Резюме)

С молекулна механика бяха проучени конформациите на молекулна пинсета (**1**), съдържаща две ароматни хирални щипки, свързани помежду си със спрегнат мостови фрагмент. Използван е MM3(π) протокол за молекулно-механично моделиране и е направено сравнение с резултати от стандартния MM3 метод, както и с полуемпирични, *ab initio* MO и DFT квантовомеханични методи. За конформационно търсене на нискоенергетични конформери е използван CONFLEX алгоритъма. Резултатите от MM3 и MM3(π) разглежданията показват, че **1** има силно предпочитание към един и същ клъстер от конформери, но геометриите на най-нискоенергетичните конформации, получени с двата протокола, се различават.