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Influence of Hexacatenar Structure on Supramolecular Organization in CT-Complexes With TNF and (−)-TAPA

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Numerical experiments to obtain theoretical data on the charge transfer complex structure, formed by the substituted benzylamine derivatives (hexacatenars) and electron acceptors—TNF or (−)-TAPA, have been performed. It is shown that the configuration and extent of the central fragment of the hexacatenar molecules influence the supramolecular organization in the modeling CT-complexes.

Keywords charge transfer complex (CT-complex); hexacatenars; electron acceptor; molecular docking; binding site

Introduction

Intermolecular charge-transfer (CT) complexes are formed when two kinds of molecules—electron donor and electron acceptor—interact. On the one hand, formation of CT-complexes leads to the increase of electric conductivity of material that creates prospects for the wide use of such systems in molecular engineering [1]. On the other hand, the spectrum of their application extends because the liquid crystal properties of the chemical compounds can be induced or modified by of the CT-complex formation [2]. The management of the molecular assembly process to get the structures with the given properties requires the knowledge of complex formation's mechanism. Experimental methods of studying of CT-complexes structure have already been applied for a long time [3]. The detailed research aimed at the determination of one molecule (acceptor) location relative to another (a molecule of the donor) neither for discotic, nor for lath-like liquid crystal compounds, were not carried out. The problem of molecule binding sites in CT-complexes searching can be solved more correctly if its solution is based on computer and mathematical modeling.

The focus of this work is numerical experiments on research of the influence of hexacatenar chemical structure on the structure of charge transfer complexes formed by them.

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Results and Discussion

The objects of the study were the CT-complexes formed by the hexacatenars (electron donors)–4,4′-[(E)-1,2-ethendiyl]bis[N-[{2,3,4-tris(butyloxy)phenyl}methylen]] benzylamine (**I**, Fig. 1a) and 4,4′- bis[(N)-2,3,4- tris (hexadecyloxy)phenyl}]benzylamine (**II**, Fig. 1b) with electron acceptor–2,4,7-trinitrofluorenon (TNF) and chiral electron acceptor–[(−)-2-(2,4,5,7-tetranitro-9-fluorenylideanaminooxy)]propionic acid ((−)-TAPA) [3]. Synthesis and identification of the compounds **I** and **II** were made in Institute of Organic Chemistry of Technical University (Berlin) under the guidance of Prof. K. Praefcke.

It was shown earlier [4, 5] that compound **I** was a nematogen and compound **II** did not have mesomorphic properties, but both formed the CT-complexes with electron acceptors–TNF and (−)-TAPA.

In our opinion, the two key factors for the numerical calculations of the CT-complex structure are: the distribution of electron density in molecules and the configuration of the central fragment of a donor-molecule. As the aliphatic fragments' extent does not play a fundamental role, it is possible to reduce the dimension of one task, replacing compound **II** with the extent alkyl fragments R=$OC_{16}H_{33}$ by compound **IIa** with R=OC_4H_9 (model compound).

Computer modeling of the CT-complex structure was carried out in two stages.

At the beginning, the microscopic characteristics of the individual investigated compounds and electron acceptors were specified by means of *ab initio* method [6, 7]. The quantum-chemical calculations have revealed that molecules of compound **I** and **IIa** (Fig. 2), TNF and (−)-TAPA (Fig. 3) have a lath-like planar form.

The distribution of the partial atom charges in molecules of the compound **I**, **IIa**, TNF and (−)-TAPA determines the potential directions of interactions at the formation of CT-complexes. In our opinion, in compound **I** and **IIa** (donors) molecule potential directions of interactions with TNF and (−)-TAPA (acceptors) are chemical groups of compound **I** and **IIa** having the most negative charges—oxygen atoms (0.7 e) in terminal alkoxy-fragments and nitrogen atoms (0.54 e) in nitrile bridge groups of donor's molecules (Fig. 2). The distribution of the charges can be accepted as the geometrical factor allowing the marking out of terminal and medial (marked out by circles in Fig. 2), terminal and central (marked out by circles in Fig. 3) fragments in molecules of compounds **I** and **IIa**.

At the second stage of computer modeling the search of the most probable binding sites of molecules in CT-complexes was realized by molecular docking method. This method is widely used in computer modeling only for two molecules binding at a complex of "albumen-ligand" for design of the new kinds of drugs in the bionanotechnology [8]. The

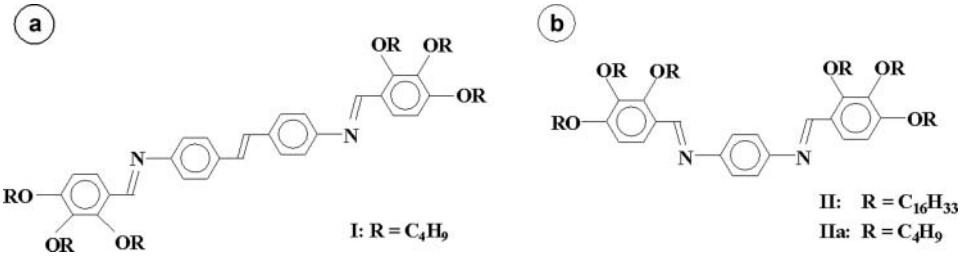

Figure 1. Structural formula of compounds **I** and **II**.

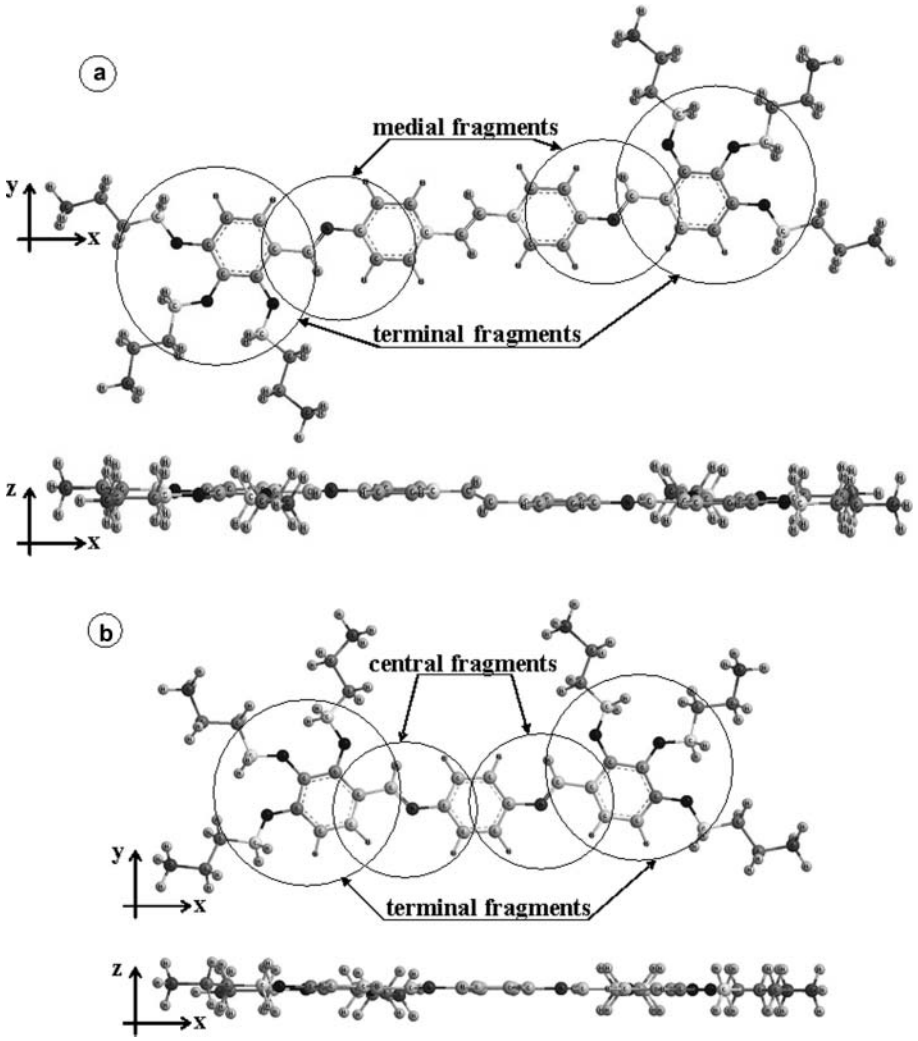

Figure 2. Optimized structures of compound **I** and **IIa** molecule in various projections. *Increase of the atom colour intensity corresponds to the increase of electronegativity.*

idea of optimum docking of one molecule with another so that forming CT-complex would have minimum energy lies in the basis of this computer method [9]. The task of the docking is the construction of complex structure model. The most simple and available variant of docking realization (flexible docking) allows only to take account of the ligand conformation mobility. The algorithm of the docking can be considered as a method of prediction of the most probable (from the power point of view) local places (sites) of binding of molecules in complexes. In our work the calculations have been made in the time interval of 1000 ps in force field MM2 by molecular dynamics. For the correct interpretation of the docking new parameter **r**–radius-vector (traced between mass centers of the structural units of the studied CT-complexes) is used as a criterion function. The estimation of mutual orientation of the donor and electron acceptor(s) in "momentary" configurations of spatial CT-complex structure was realized through every 0.5 ps during all calculation time interval.

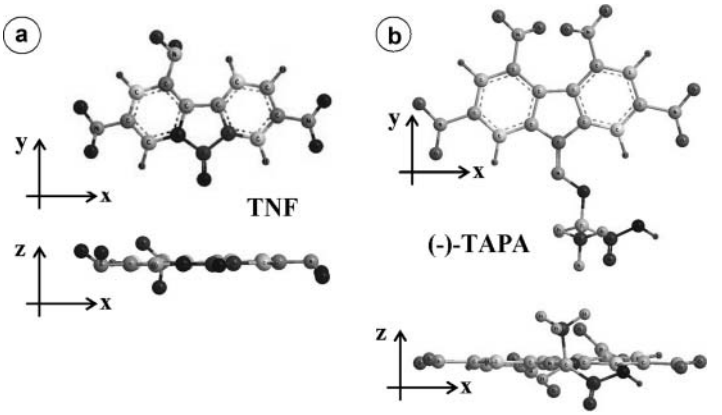

Figure 3. Optimized structures of the TNF and (−)-TAPA molecule in various projections. *Increase of the atom colour intensity corresponds to the increase of electronegativity.*

The CT-complexes of compound **I** and **IIa** with TNF and (−)-TAPA in molecular correlation donor:acceptor 1:1 and 1:2 were used as starting models for calculations by molecular docking method.

All results of calculations testified that TNF and (−)-TAPA molecules were in planes, that are coplanar to molecule-donor plane (compounds **I** or **IIa**).

In the modeling of CT-complexes of compound **I** with TNF (1:1) a binding site was the acceptor location over a surface of a molecule of compound **I** on distance $\mathbf{r} = 9.68$ Å (Fig. 4a). The docking of the two TNF molecules (1:2) has revealed their orientation in binding site with compound **I** (Fig. 4b) on $\mathbf{r_1} = 10.96$ Å and $\mathbf{r_2} = 9.62$ Å. Thus the average distance (R) between the mass centres of acceptor molecules was 18.84 Å.

The binding site of the TNF with compound **IIa** is characterized by value of estimated parameter $\mathbf{r} = 5.72$ Å (Fig. 5a) in modeling CT-complexes (1:1). For two molecules of TNF acceptor in CT-complexes 1:2 the positions of the TNF over a molecule of compound **IIa** with $\mathbf{r_1} = 8.45$ Å and $\mathbf{r_2} = 6.05$ Å, correspondingly, (Fig. 5b) are energetically favorable. Equilibrium value R in the binding site is 12.39 Å.

Thus, the optimal docking of TNF acceptor molecules with compound **I** and **IIa** was concluded in location of the TNF (one and/or two molecules) over terminal parts (Fig. 2 and 3) of the molecules of both compounds. Distinction in the abovementioned statistical data of docking results is explained by considerably smaller extent of a model compound **IIa** center fragment in comparison with the center fragment of compound **I**.

In modeling CT-complexes (1:1 and 1:2), formed by compound **I** with a chiral electron acceptor (−)-TAPA, the coordination (Fig. 6) of the acceptor is energetically favorable over medial fragments of donor molecules (Fig. 2). For one molecule of an acceptor the binding site with compound **I** is characterized by $\mathbf{r} = 6.81$ Å (Fig. 6a). Values of the estimated parameter for positions of two (−)-TAPA molecules in the CT-complex 1:2 are $\mathbf{r_1} = 7.64$ Å, $\mathbf{r_2} = 4.57$ Å (Fig. 6b). The distance between mass centres of the acceptor molecules in a binding site has accepted average value 9.52 Å.

In CT-complexes of the model compound **IIa** with an electron acceptor (−)-TAPA (1:1) a binding site was the acceptor location over the surface of the compound **IIa** molecule at the distance $\mathbf{r} = 5.33$ Å (Fig. 7a). The docking of the two (−)-TAPA molecules (1:2) has revealed their orientation in binding sites with compound **IIa** (Fig. 7b) at $\mathbf{r_1} = 8.08$ Å and $\mathbf{r_2} = 5.81$ Å. The distance between the mass centres of acceptor molecules has R = 11.77 Å.

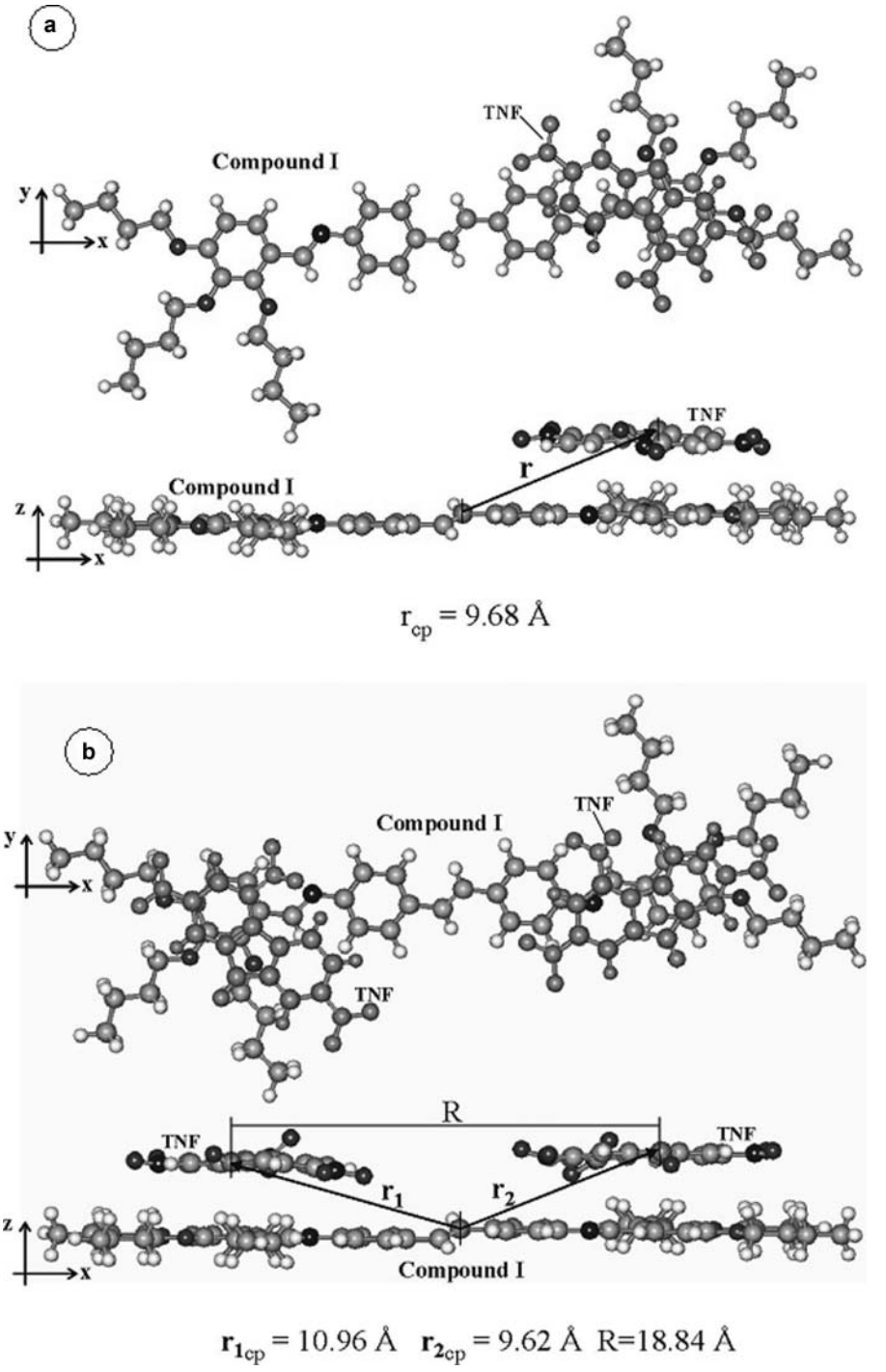

Figure 4. Equilibrium geometry of CT-complexes of compound **I** and TNF.

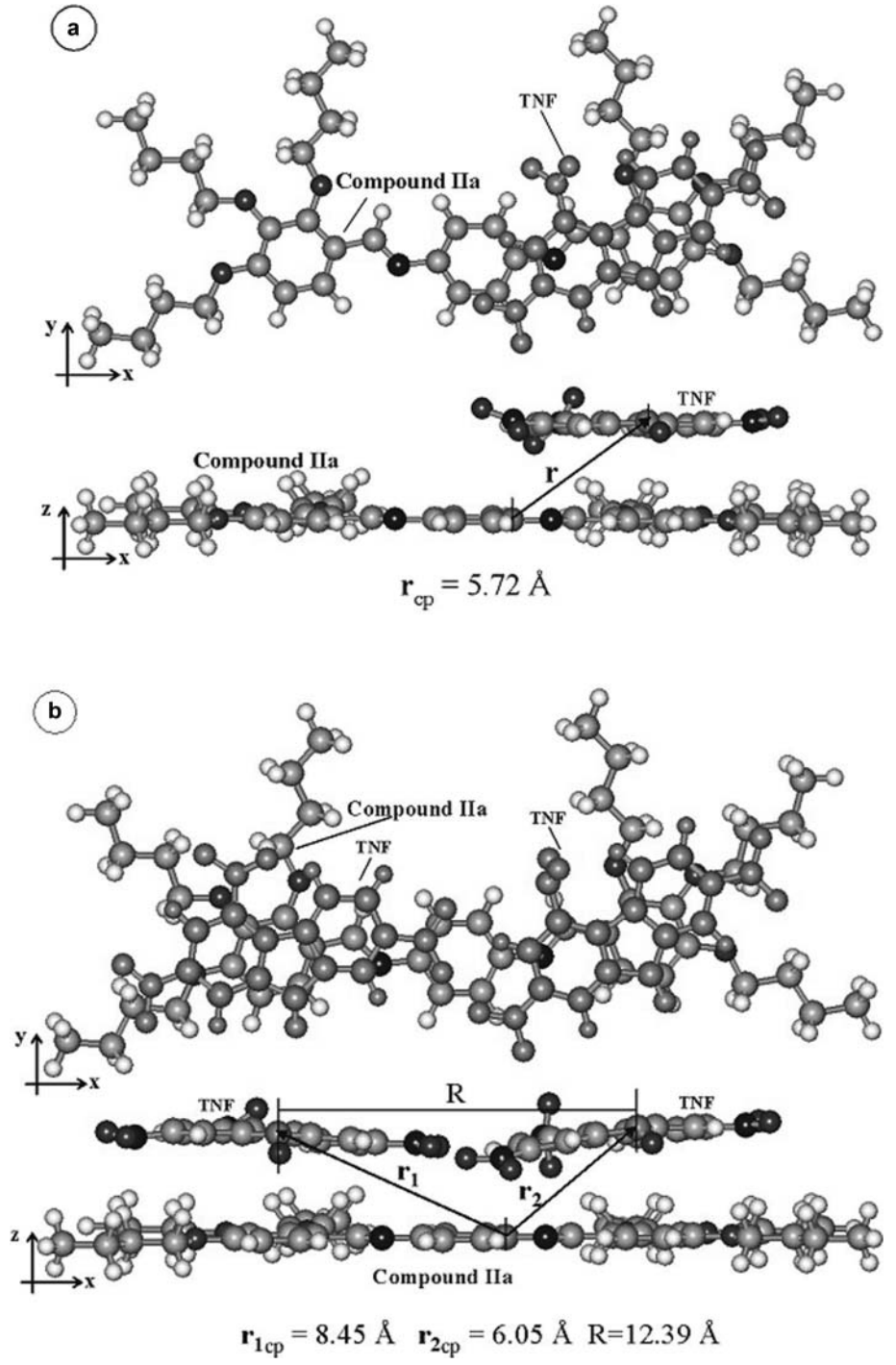

Figure 5. Equilibrium geometry of CT-complexes of compound **IIa** and TNF.

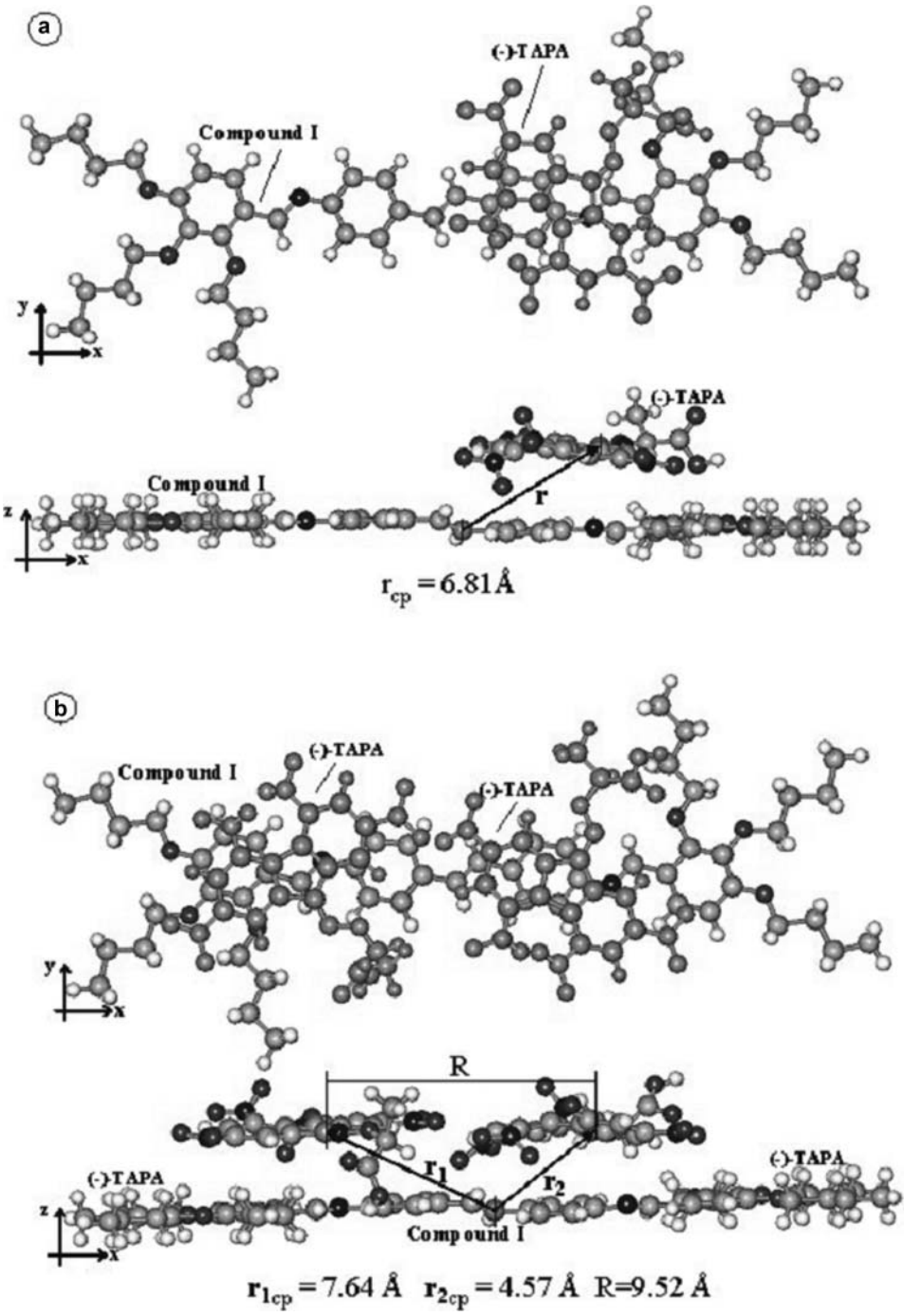

Figure 6. Equilibrium geometry of CT-complexes of compound **I** and (−)-TAPA.

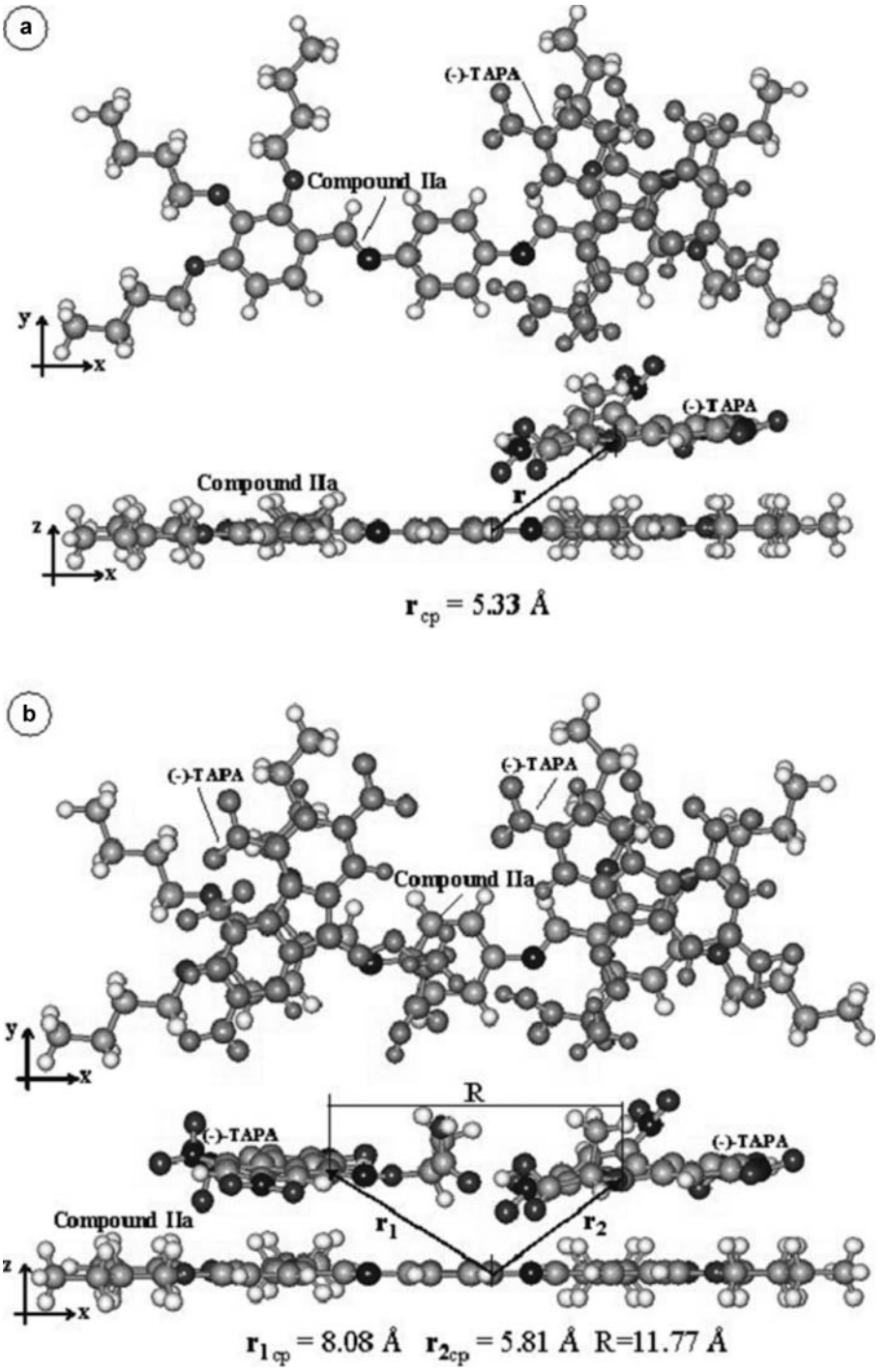

Figure 7. Equilibrium geometry of CT-complexes of compound **IIa** and (−)-TAPA.

Thus, the docking of (−)-TAPA in CT-complexes (1:1 and 1:2) with compound **I** has revealed the binding sites over a medial part of a donor molecule. On the contrary, for one and/or two (−)-TAPA molecules in CT-complexes with compound **IIa** the acceptor location over terminal fragments of donor molecules (Fig. 3) is energetically favorable. Thus, the acceptor molecule is oriented so, that it is chiral fragment settles down over the central part of a compound **IIa** molecule. Possibly, on the one hand, the various extent of the central fragment of molecules of the electron donors and the different configuration of the compound **I** and **IIa** molecules lead to such difference in binding sites. On the other hand, the difference may be connected with the feature of a chemical structure of a molecule (−)-TAPA: the chiral substitute is an additional steric factor influencing the mutual orientation of molecules.

Conclusions

The docking is successfully used for the description of binding sites of the donor molecules and electron acceptor molecules in CT-complexes of the low-molecular organic compounds for the first time.

Theoretical data about the preferable location of electron acceptors TNF and (−)-TAPA relatively to the electron donors - the substituted benzylamine derivatives—in CT-complexes were obtained. Models of CT-complex structure formed by compound **I** and **IIa** with electron acceptors TNF and (−)-TAPA were constructed.

It is shown that hexacatenar structure, namely, the configuration of the central fragment of a molecule and its extent influence the supramolecular organization of the substituted benzylamine derivative in CT-complexes with acceptors TNF and (−)-TAPA.

The docking for all modeling charge transfer complexes in the correlation donor:acceptor 1:2 has proven the impossibility of the third molecule of an acceptor (TNF and (−)-TAPA) to orient over the surface of the donor.

Acknowledgment

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