

## АНАЛИЗ ЧУВСТВИТЕЛЬНОСТИ МЕТОДА ГАЗОВОЙ ЭЛЕКТРОНОГРАФИИ К ОПРЕДЕЛЕНИЮ КОНФОРМАЦИОННОГО СОСТАВА ФЕНИЛ- И ТИОФЕНИЛЗАМЕЩЕННЫХ АЗА-BODIPY: ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ

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*С помощью квантово-химических расчетов при использовании метода функционала плотности (гибридный функционал B3LYP) изучено конформационное многообразие 1,3,5,7-тетрафенил-аза-BODIPY и 1,3,5,7-тетра(2-тиофенил)-аза-BODIPY. Введение в структуру аза-BODIPY четырех групп-заместителей приводит к повороту и сопутствующему выходу данных групп из плоскости гетероцикла. Углы поворота фенильной и тиофенильной групп в рассмотренных молекулах составляют около 30° и 17°, соответственно. С помощью квантово-химических расчетов B3LYP/6-31G\* и B3LYP/cc-pVTZ найдено четыре конформера для фенилзамещенного аза-BODIPY и 30 конформеров для тиофенилзамещенного аза-BODIPY. Относительные энергии некоторых конформеров достаточно малы, поэтому их возможное присутствие в паре необходимо учитывать при обработке экспериментальных электронографических данных. В настоящей работе исследована чувствительность метода газовой электронографии к структурным изменениям, вызванным различным положением фенильных и тиофенильных заместителей относительно друг друга и относительно остова аза-BODIPY. Сопоставлены теоретические функции радиального распределения  $f(r)$  для конформеров двух рассмотренных молекул. Межъядерные расстояния между химически связанными атомами могут быть надежно определены из экспериментальных электронографических данных. Однако определение взаимных ориентаций соседних групп по отношению друг к другу находится на пределе возможностей метода газовой электронографии. На основании экспериментальных данных можно различить конформеры 1,3,5,7-тетра(2-тиофенил)-аза-BODIPY с отличными друг от друга взаимными расположениями атомов серы. Использование результатов квантово-химических расчетов, полученных при использовании различных наборов базисных функций (6-31G\* и cc-pVTZ), позволяет получить сходные друг с другом изображения функций радиального распределения  $f(r)$ , а значит и одинаковые выводы о возможности метода газовой электронографии определять конформационный состав.*

**Ключевые слова:** газовая электронография, теория функционала плотности, конформационный анализ, аза-BODIPY

## ANALYSIS OF THE SENSITIVITY OF THE GAS ELECTRON DIFFRACTION METHOD TO THE DETERMINATION OF THE CONFORMATIONAL COMPOSITION OF PHENYL AND THIOPHENYL SUBSTITUTED AZA-BODIPY: THEORETICAL STUDY

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*Conformational manifold of 1,3,5,7-tetraphenyl-aza-BODIPY and 1,3,5,7-tetra(2-thiophenyl)-aza-BODIPY was studied by B3LYP calculations. The addition of four cyclic groups to the aza-BODIPY core defines the non-planarity of the molecule and movement of the substituents from the heterocycle plane. The rotation angles of the phenyl and thiophenyl groups in the molecules are about 30° and 17°, respectively. For phenyl-substituted aza-BODIPY four conformers were found using quantum chemical calculations (B3LYP/6-31G\* and B3LYP/cc-pVTZ), for thiophenyl-substituted aza-BODIPY – 30 conformers. Relative energies of some conformers are quite low, therefore they should be taken into account in the treatment of the gas electron diffraction (GED) experimental data. In current work the sensitivity of the GED method to the structural changes induced by different positions of phenyl and thiophenyl substituents relative to the aza-BODIPY core and each other was examined. Model radial distribution curves  $f(r)$  for all conformers were compared. It demonstrates that the bond distances can be reliably determined from experimental data, while the refinement of mutual orientations of neighboring groups relating to each other is at the limit of the possibilities of the GED method. Based on experimental data, it is possible to distinguish 1,3,5,7-tetra(2-thiophenyl)-aza-BODIPY conformers, which differ in the mutual arrangement of sulfur atoms. The use of the results of various quantum chemical calculations leads to the same conclusions about the possibility of the gas electron diffraction method to determine the conformational composition.*

**Key words:** gas electron diffraction, DFT, conformational analysis, aza-BODIPY

### Для цитирования:

Погонин А.Е., Постникова Д.А., Шагурин А.Ю., Марфин Ю.С., Гиричев Г.В. Анализ чувствительности метода газовой электронографии к определению конформационного состава фенил- и тиофенилзамещенных аза-BODIPY: теоретическое исследование. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 10. С. 29–37. DOI: 10.6060/ivkkt.20226510.6687.

### For citation:

Pogonin A.E., Postnikova D.A., Shagurin A.Yu., Marfin Yu.S., Girichev G.V. Analysis of the sensitivity of the gas electron diffraction method to the determination of the conformational composition of phenyl and thiophenyl substituted aza-BODIPY: theoretical study. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.]*. 2022. V. 65. N 10. P. 29–37. DOI: 10.6060/ivkkt.20226510.6687.

## INTRODUCTION

One of the main problems of modern chemistry is the molecular design of chemical structures. The

emergence of new fields of practical application of BODIPY derivatives as parts of sensor devices and solar cells, materials for nonlinear optics, medicine [1, 2], etc. requires a fundamental study of the relationship

between the structure, physicochemical properties, and reactivity in various processes. BODIPY derivatives are studied by almost all physicochemical methods: a variety of spectroscopies in the visible region, including UV-Vis spectroscopy [3-5], transient absorption [6-8] and multiphoton absorption [9-12], as well as IR spectroscopy [13-16], NMR spectroscopy [17-20], EPR spectroscopy [21-23], differential scanning calorimetry [24-26], cyclic voltammetry [27-29] and X-ray diffraction (XRD) analysis [30-32]. Moreover, a large number of works [13,33,34] are devoted to the quantum chemical (QC) calculations of BODIPYs structures. At the same time, it is surprising that there are no data on the structure of these molecules in the gas phase. Structural information about free molecules is of particular importance, since in the gas phase there are no collective interactions that intro-

duce significant distortions of the molecules, as is the case in the condensed state. By studying free molecules, one can establish with the greatest certainty the individual properties of compounds, describe the fine details of their geometric and electronic structure and nuclear dynamics. The most common experimental method for determination of gas-phase structures is gas electron diffraction (GED) [35, 36]. Molecular structures determined by GED can be used for the development of the corresponding subsections of stereochemistry and for the assessment of the performance of various theoretical methods [37, 38]. However, in the case of large molecules structural refinement of GED data is usually a non-trivial procedure [39-41]. The cyclic compounds with various substituents can exhibit different types of non-planar distortions and this circumstance brings the additional difficulties in the structural analysis.

The sensitivity of the GED method to the determination of the conformational composition of compounds bearing ethyl and halogenophenyl substituents was examined [38, 42-44] on the example of porphyrins. In order to assess the ability of the GED method to distinguish between different conformations of molecules, it is proposed to compare the model curves of the radial distribution  $f(r)$  for appropriate conformations using the results of QC calculations. GED method did not allow solving the confor-

mational problem of the ethyl and halogenophenyl substituted porphyrins in a gas phase [38, 42-44], but at the same time GED proved to be sensitive to the situation regarding position of the ethyl groups relatively to the macroheterocycle. For 5,10,15,20-tetrakis(40-fluorophenyl)porphyrin, the results based on this theoretical approach [38] were obtained in good qualitative and even quantitative agreement with the results described in subsequent experimental GED work [44].

The present work continues the studies devoted to determining the sensitivity of the GED method to the determination of the conformational composition of cyclic compounds. The objects of the current study are 1,3,5,7-tetraphenyl-aza-BODIPY (**1**) and 1,3,5,7-tetra(2-thiophenyl)-aza-BODIPY (**2**) (Fig. 1).

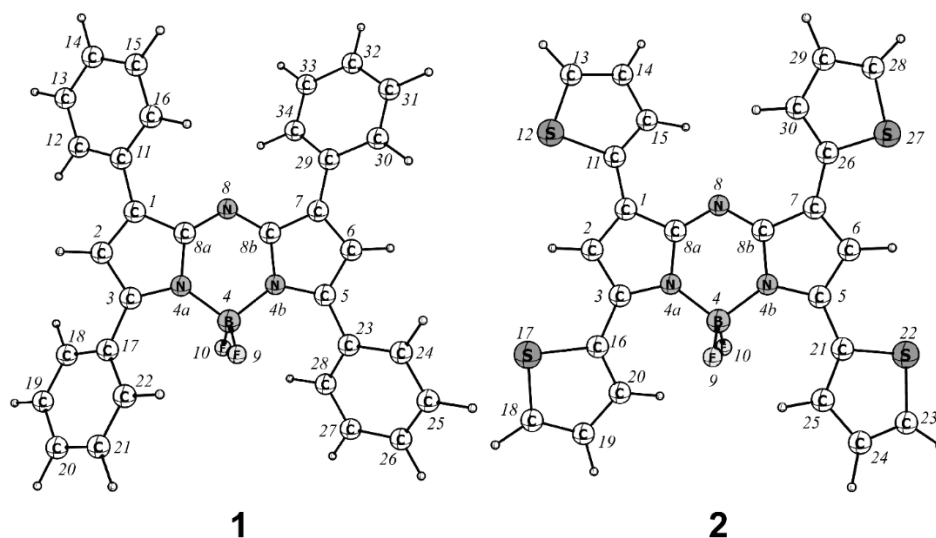


Fig. 1. Molecular structure and atom numbering in molecules **1** and **2**

Рис. 1. Молекулярная структура и нумерация атомов для молекул **1** и **2**

## COMPUTATIONAL DETAILS

QC calculations of molecular geometries and Hessians of the **1** and **2** were performed using the Gaussian 09 program package [45] in the framework of DFT method with the functional B3LYP. Calculations were carried out using following basis sets –  $6-31G^*$  [46-49] and  $cc-pVTZ$  [50,51] for all atoms. The basis sets were taken from the Basis Set Exchange software [52-54]. The optimized structures from QC calculations are given in the Supplementary materials.

Vibrational amplitudes and vibrational corrections to nuclear distances were calculated on the base of force field obtained from quantum chemical calculations with the use VibModule program [55] for the temperature  $T = 430$  K. In calculations for confor-

mations (VI – for **1**; Vaa, Vab, Vba, Vbb – for **2**), the imaginary vibration frequencies were taken as real (35 and 21 cm<sup>-1</sup> (according to B3LYP/6-31G\* and B3LYP/cc-pVTZ calculations, respectively) – for **1**; 58, 20, 60, 21 cm<sup>-1</sup> (according to B3LYP/6-31G\* calculations) – for Vaa, Vab, Vba, Vbb of **2**, respectively).

Calculations of the model radial distributions curves  $f(r)$  were performed in the modified KCED-35 program, which is similar to the program described in the paper [56]. The difference curves  $\Delta f(r)$  were calculated relative to the curve corresponding to conformer with minimal energy:  $\Delta f(r) = f_j(r) - f_{\text{reference}}(r)$ . The deviation of the  $j$ -th curve from the reference curve was characterized by disagreement factor ( $R_{f,j}$ ) between the theoretical molecular scattering intensities corresponding to different models:

$$R_{f,j} = \sqrt{\frac{\sum_{i=1}^N (sM(s_i)_{\text{reference}} - sM(s_i)_{\text{model } j})^2}{\sum_{i=1}^N (sM(s_i)_{\text{reference}})^2}} \cdot 100\%$$

where  $sM(s_i)_{\text{reference}}$  – theoretical molecular scattering intensities for conformer with minimal energy: for **1** – conformer IV, for **2** – conformer Iaa;  $sM(s_i)_{\text{model } j}$  – theoretical molecular scattering intensities for corresponding conformer.

## RESULTS AND DISCUSSION

Conformational multiformity of **1** and **2** is associated with the possible rotation of substituent groups around the C-C bonds. Rotation barriers of phenyl and thiophenyl are around 23 and 35 kJ·mol<sup>-1</sup>, respectively [34]. The molecules are non-planar due to the movement of the substituents out of the heterocycle plane. For **1** the torsional angles  $\tau(\text{C}_2\text{-C}_3\text{-C}_{17}\text{-C}_{18})$  and  $\tau(\text{C}_2\text{-C}_1\text{-C}_{11}\text{-C}_{12})$  are about 34° and 28°, respectively; for **2** –  $\tau(\text{C}_2\text{-C}_3\text{-C}_{16}\text{-S}_{17}) \approx \tau(\text{C}_2\text{-C}_1\text{-C}_{11}\text{-S}_{12}) \approx 17^\circ$ . Conformations of **1** differ by mutual orientations of neighboring phenyl groups relating to each other (Fig. 2). According to the QC calculations, structures I, II, IV and V (Fig. 2) of molecule **1** correspond to minima on the potential energy surface (PES). Conformation VI corresponds to the saddle point on the PES with the imaginary frequencies describing rotation of phenyl groups in positions 1 and 7 (Fig. 2). It should be noted that the structure III transforms to conformer I within geometry optimization. Conformer IV possesses the lowest energy (Table 1). QC calculations with different basis sets give the same qualitative picture of the relative energies of the considered structures (Table 1).

In order to assess the ability of the GED method to distinguish between conformations of molecule **1**, the simulated radial distributions curves  $f(r)$  were compared (Fig. 3, Fig. S1). Bond lengths and

bond angles are almost the same values in all conformers of **1**, thereby  $\Delta f(r)$  for considered structures differ only slightly. Considered models should equally describe the experimental data. Bond lengths and bond angles can be refined with a typical accuracy of GED method. Therefore, the geometry structures of aza-BODIPY core and phenyl rings can be reliably determined. It should be noted that the simulated  $f(r)$  and  $\Delta f(r)$  obtained using B3LYP/6-31G\* and B3LYP/cc-pVTZ calculations are in good agreement with each other (Fig. 3, Fig. S1). Although it is worth noting a noticeable increase in the  $R_f$  for conformer V (for B3LYP/cc-pVTZ –  $R_f = 1.97\%$ , for B3LYP/6-31G\*  $R_f = 4.59\%$ ). The reason is the overestimated values of the vibrational corrections, since the frequency values are underestimated in the QC calculations. In case of results from B3LYP/6-31G\* calculations for conformer V, the vibrational frequency of rotations of phenyls is 6.5 cm<sup>-1</sup>. According to other QC calculations of conformers of molecule **1**, minimal frequency is not lower than 14 cm<sup>-1</sup>.

Table 1

Relative energies of conformers I, II, IV, III and V, conformation VI of molecule 1

Таблица 1. Относительные энергии конформеров I, II, III, IV, V и конформации VI молекулы 1

Structure	I	II	III	IV	V	VI
Symmetry	C <sub>2</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>s</sub>	C <sub>s</sub>
$\Delta E$ , kJ·mol <sup>-1</sup> B3LYP/6-31G*	0.60	2.25	-	0.00	3.21	7.36
$\Delta E$ , kJ·mol <sup>-1</sup> B3LYP/cc-pVTZ	0.74	2.42	-	0.00	2.55	6.87

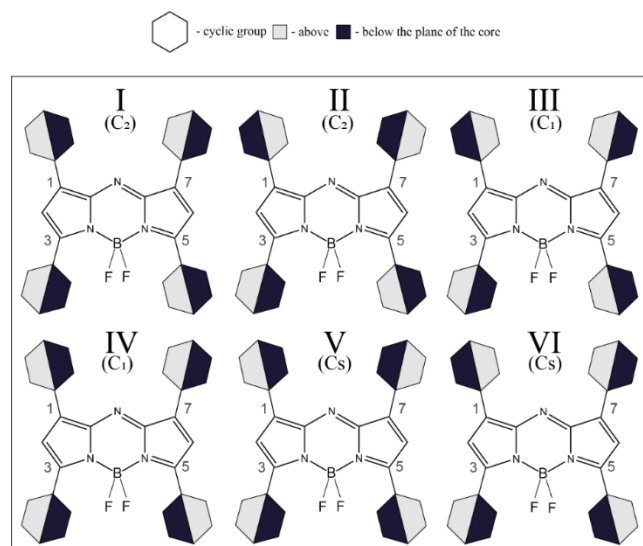


Fig. 2. Conformation models of aza-BODIPY derivatives substituted by cyclic groups in 1, 3, 5, 7-positions

Рис. 2. Модели конформаций производных аза-BODIPY с циклическими группами-заместителями в 1, 3, 5, 7-положениях

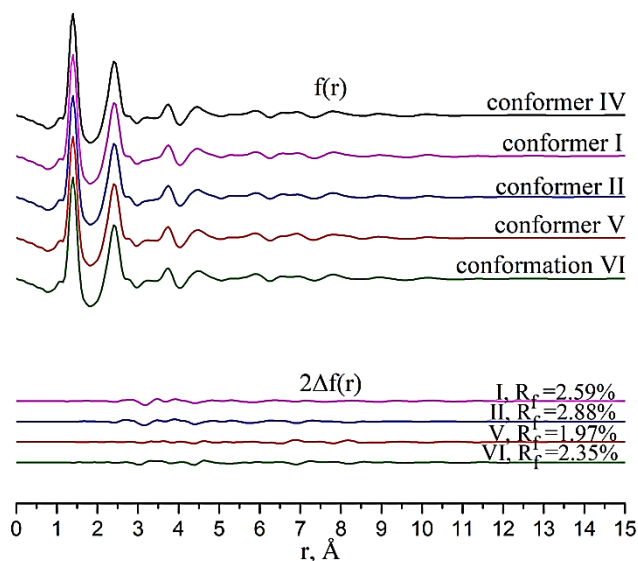


Fig. 3. Comparison of theoretical radial distribution functions  $f(r)$  of molecule **1**. Differences functions  $\Delta f(r)$  were calculated concerning conformer IV (Fig. 2). Molecular parameters were calculated at B3LYP/cc-pVTZ theory level

Рис. 3. Сравнение теоретических функций радиального распределения  $f(r)$  для **1**. Разностные функции  $\Delta f(r)$  рассчитаны относительно конформера IV (Рис. 2). Молекулярные параметры рассчитаны в приближении B3LYP/cc-pVTZ

Conformational multiformity of the molecule **2** is additionally complicated by the presence of a sulfur atom in the cyclic substituent group, i.e. by different arrangement of sulfur atoms with respect to the center of the molecule (Fig. 4). Given the presence of four 2-thiophenyl groups, 10 models need to be considered (Fig. 5). By adding the factor of groups rotation discussed earlier in example of **1** (Fig. 2), the number of models to consider increases to 60 (models  $NXX$ , where  $N = I/II/III/IV/V/VI$  (see Fig. 2),  $X = a/b/c$  (see Fig. 5)). According to the QC calculations, structures  $IXX$ ,  $IIXX$  and  $IVXX$  (Table 2) correspond to minima on the PES. The structures  $Vaa$ ,  $Vab$ ,  $Vba$ ,  $Vbb$  of  $C_2$  symmetry corresponds to the saddle points on the PES ( $\Delta E = 5.97, 8.55, 20.03$  and  $23.22 \text{ kJ}\cdot\text{mol}^{-1}$ , respectively) with the imaginary frequencies describing rotation of phenyl groups in positions *1* and *7*. Within geometry optimization other models transform to the structures noted above. The most energetically preferable conformer is  $Iaa$ .

As described above for molecule **1**, various variants of the mutual orientation of thiophenyl groups located outside the plane of the aza-BODIPY core ( $IIN \rightarrow IIIN \rightarrow IVNN$ , Fig. 2) do not lead to a significant change in the  $f(r)$ . According to the difference curves  $\Delta f(r)$ , such conformers will be indistinguishable in the GED experiment conditions (for ex-

ample,  $Iaa, IIaa, IVaa$ , see Fig. S2-4). Although some conformers differing in the mutual arrangement of sulfur atoms inside the molecule (Fig. 4) can be distinguished (Fig. 6). There are several reasons for this. Foremost, there are significant changes in the distances between nonbonded atoms, primarily  $S\cdots S$ ,  $S\cdots N$  and  $S\cdots F$  (Table S1). It is worth noting here that sulfur atoms have higher scattering ability as compared to other atoms. In connection with it a change in distances should lead to bigger changes of radial distribution curves. Secondly, rotation of the thiophenyl groups can lead to some changes in the structure. According to the B3LYP/cc-pVTZ calculations, the transition  $Iaa \rightarrow Ibb$  is accompanied by an increase in distances  $r_e(C_{20}-C_{16})$  by  $0.006 \text{ \AA}$  and by a decrease in distances  $r_e(S_{17}-C_{16})$ ,  $r_e(S_{12}-C_{11})$ ,  $r_e(B_4-F_{10})$  by  $0.009 \text{ \AA}$ ,  $0.005 \text{ \AA}$ ,  $0.003 \text{ \AA}$ , respectively. It is worth noting a slight difference in the  $f(r)$  obtained for the conformers  $Iaa$  and  $Iac$  ( $R_{f,Iac} = 3.13\%$ , Fig. 6). The GED method is more sensitive to different arrangements of thiophenyl fragments located in positions 3 and 5 than to different arrangements of the groups located in positions 1 and 7 (Fig. 6).

Analysis of the sensitivity of the GED method to the determination of the conformational composition using 6-31G\* and cc-pVTZ basis sets confirms that they give the same results. This fact can be used in preparation for the GED investigation of objects with many possible conformers in order to minimize computational time.

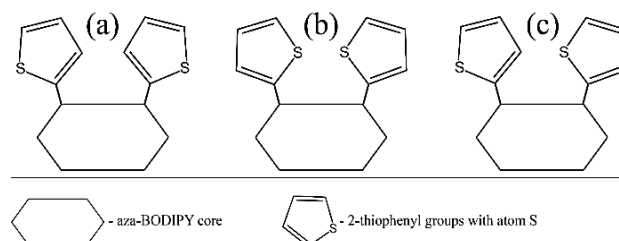


Fig. 4. Conformation models of aza-BODIPY derivatives substituted by thiophenyl groups in 1, 3, 5, 7-positions: (a) sulfur atoms in thiophenyl groups are oriented by "outer" direction with respect to center of molecule; (b) sulfur atoms in thiophenyl groups are directed by "inner" direction with respect to center of molecule; (c) one sulfur atom in one thiophenyl group is directed by "inner" direction, another sulfur atom in another group—by "outer"

Рис. 4. Модели конформаций производных аза-BODIPY с тиофенильными группами-заместителями в 1, 3, 5, 7-положениях: (а) атомы серы в тиофенильных группах ориентированы «наружу» по отношению к центру молекулы; (б) атомы серы в тиофенильных группах направлены «внутри» по отношению к центру молекулы; (с) один атом серы в одной тиофенильной группе направлен «внутри», другой атом серы в другой группе – «наружу»

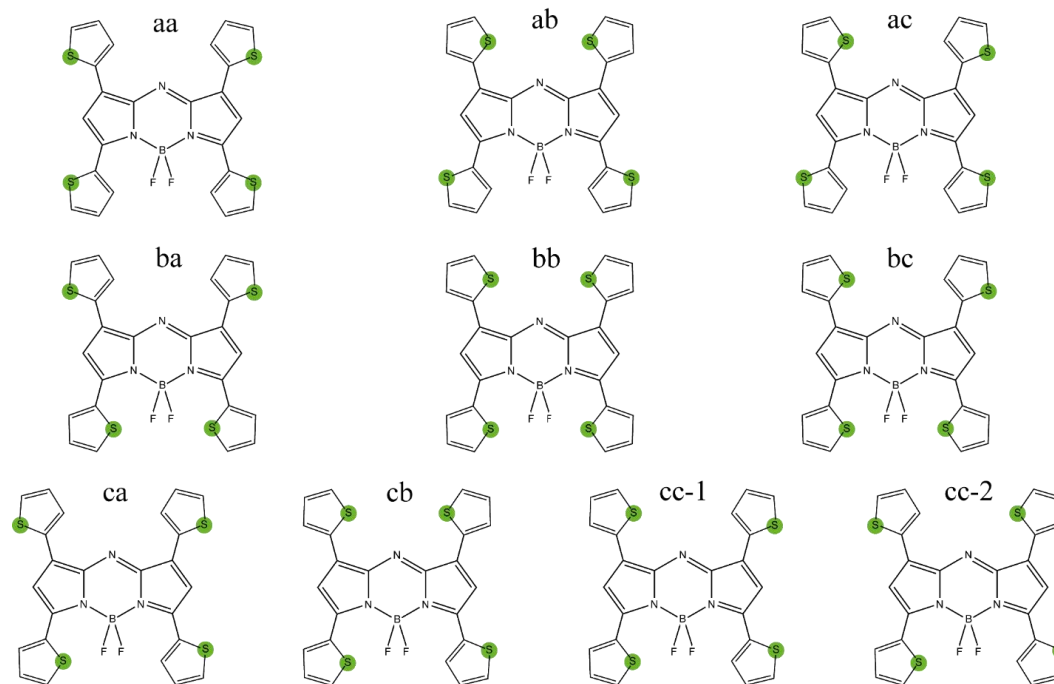


Fig. 5. Conformation models of **2**. The first letter (a/b/c - see Fig. 4) indicates the arrangement of neighboring thiophenyl groups in positions 3, 5, the second letter indicates the arrangement of neighboring thiophenyl groups in positions 1, 7

Рис. 5. Модели конформаций молекулы **2**. Первая буква (a/b/c – см. Рис.4) указывает на вариант расположения соседних тиофенильных фрагментов в положениях 3, 5, вторая буква - на вариант расположения соседних тиофенильных фрагментов в положениях 1, 7

Table 2

Relative energies of conformers of molecule **2**  
Таблица 2. Относительные энергии конформеров молекулы **2**

	model NXX	Naa	Nab	Nac	Nba	Nbb	Nbc	Nca	Ncb	Ncc -1	Ncc-2
Symmetry		C <sub>2</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>2</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>	C <sub>1</sub>
$\Delta E$ , kJmol <sup>-1</sup> 6-31G*	IXX	0.00	6.05	1.40	14.63	21.19	16.30	6.99	13.31	8.70	8.35
$\Delta E$ , kJmol <sup>-1</sup> cc-pVTZ	IXX	0.00	5.18	1.33	14.81	20.49	16.40	7.13	12.56	8.73	8.40
$\Delta E$ , kJmol <sup>-1</sup> 6-31G*	IIXX	0.33	6.29	1.65	15.11	21.64	16.72	7.43	13.67	9.10	8.67
$\Delta E$ , kJmol <sup>-1</sup> 6-31G*	IVXX	1.43	7.41	2.61	15.46	22.02	17.22	8.03	14.30	9.56	9.48

According to the data of the present study, the structural parameters in the considered molecules change slightly upon rotations of phenyl and thiophenyl groups. The refinement of mutual orientations of neighboring groups relating to each other (models I-VI) is at the limit of the abilities of the GED method. In the case of molecule **2**, it is quite possible to distinguish from each other conformers with different mutual arrangement of sulfur atoms in relation to each other (models aa-cc). The changes in the non-bonded distances with sulfur atoms influence the model molecular intensities  $sM(s)$  and therefore an attempt can be made to distinguish between the conformers based on the experimental GED data.

At the same time, in both cases, bond lengths and bond angles can be refined with a typical accuracy of GED method.

#### SUPPLEMENTARY MATERIALS

The following are available online: Fig. S1. Comparison of theoretical radial distribution functions  $f(r)$  of molecule **1**. Fig. S2-S5. Comparison of theoretical radial distribution functions  $f(r)$  of conformers and conformations of molecule **2**. Table S1. Comparison of internuclear distances (Å) for conformers Iaa, Iab, Ibb of molecule **2** from B3LYP/cc-pVTZ calculations. Additionally, optimized structures from B3LYP/6-31G\* and B3LYP/cc-pVTZ calcula-

tions are given in Supplementary materials. Supplementary materials to this article can be found online at <http://journals.isuct.ru/ctj/>.

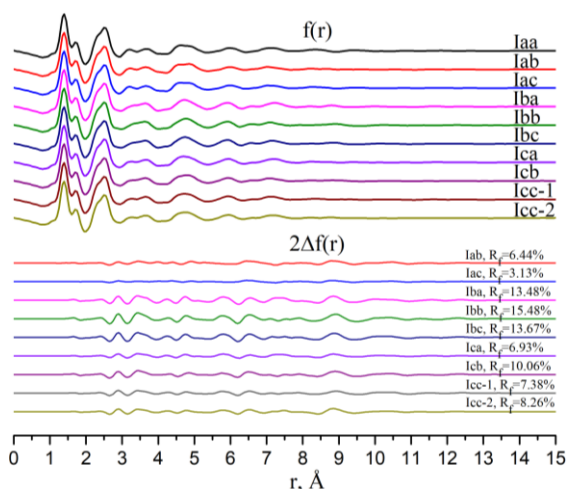


Fig. 6. Comparison of theoretical radial distribution functions  $f(r)$  of molecule **2**. Differences functions  $\Delta f(r)$  were calculated concerning conformer Iaa (Fig. 2, 5). Molecular parameters were calculated at B3LYP/cc-pVTZ theory level

Рис. 6. Сравнение теоретических функций радиального распределения  $f(r)$  для **2**. Разностные функции  $\Delta f(r)$  рассчитаны относительно конформера Iaa (Рис. 2, 5). Молекулярные параметры рассчитаны в приближении B3LYP/cc-pVTZ

#### ACKNOWLEDGEMENTS

The reported study was funded by the grant of the President of the Russian Federation (project MK-5965.2021.1.3).

The study was carried out using the resources of the Center for Shared Use of Scientific Equipment of the ISUCT (with the support of the Ministry of Science and Higher Education of Russia, grant No. 075-15-2021-671).

The authors declare the absence a conflict of interest warranting disclosure in this article.

Данное исследование выполнено за счет гранта Президента Российской Федерации (проект MK-5965.2021.1.3).

Исследование выполнено с использованием ресурсов Центра коллективного пользования научной аппаратурой ИГХТУ (при поддержке Минобрнауки России, грант № 075-15-2021-671).

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

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Поступила в редакцию 07.06.2022

Принята к опубликованию 23.06.2022

Received 07.06.2022

Accepted 23.06.2022