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DFT ИЗУЧЕНИЕ МОЛЕКУЛЯРНОЙ СТРУКТУРЫ 5,10,15,20-ТЕТРАКИС(4'-ГАЛОГЕНФЕНИЛ)ПОРФИНОВ И ИХ ИЗОМЕРОВ

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Настоящая статья является продолжением работ по установлению чувствительности электронографического метода в отношении определения конформационного состава макроциклических молекул, осложненных введением групп-заместителей различной природы. С помощью квантово-химических расчетов (метод DFT, функционал B3LYP) изучено конформационное многообразие 5,10,15,20-тетракис(4′-X)фенилпорфинов (n-4C_6H_4X-H_2P: X = F, Br). Рассмотренные конформеры отличаются положением -4C_6H_4X групп относительно макроцикла. Относительные энергии конформеров C_6H_4F-H_2P были вычислены с использованием различных базисных наборов с целью подбора варианта, наиболее оптимального по соотношению «качество расчета/вычислительная стоимость». Согласно результатам расчетов наиболее энергетически выгодной структурой n-4C_6H_4X-H_2P является конформер симметрии C_{2v}. В то же время, относительные энергии других конформеров весьма малы, поэтому их возможное присутствие в паре необходимо учитывать при обработке экспериментальных электронографических (ЭГ) данных. Замена атомов F на атомы Br при переходе 4C_6H_4F-H_2P→4C_6H_4Br-H_2P не приводит к значительным изменениям строения порфиринового остова. Выполнен анализ чувствительности метода газовой электронографии к структурным изменениям, обусловленным различным положением галогенфенильных заместителей. Сопоставлены теоретические функции радиального распределения f(r) конформеров n-4C_6H_4X-H_2P, а также мета- и орто-изомеров – м-4C_6H_4X-H_2P и о-4C_6H_4X-H_2P. Результаты моделирования свидетельствуют о возможности надежного экспериментального определения расстояний между химически связанными атомами, в то время как уточнение положения галогенфенильных заместителей относительно макроциклического остова молекулы находится на пределе возможностей метода. На основе экспериментальных данных можно надежно различить мета- и орто- изомеры 4C_6H_4X-H_2P, в особенности, в случае бромзамещенных фенильных групп.

Ключевые квантово-химические расчеты, теория функционала плотности, порфирин, конформационный анализ

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DFT STUDY OF MOLECULAR STRUCTURE OF 5,10,15,20-TETRAKIS(4′-HALOGENOPHENYL)PORPHYRINS AND THEIR ISOMERS

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Conformational manifold of 5,10,15,20-tetrakis(4′-halogenophenyl)porphyrins (p-4C_6H_4X-H_2P; X=F, Br) was studied by DFT calculations (functional B3LYP). The conformers are different by positions of -4C_6H_4X groups relative to the macrocyclic core. Relative energies of the conformers of 4C_6H_4F-H_2P were calculated with use of different basis sets in order to find the optimal ratio «quality/ computational cost». According to the results of the calculations, conformers of C_{2V} symmetry are the most energetically favorable. However, relative energies of other conformers are quite low, therefore they should be taken into account at the treatment of the gas-phase electron diffraction (GED) experimental data. The sensitivity of the GED method to structural changes induced by different relative positions of halogenophenyl substituents was examined. Model radial distribution curves f(r) for conformers of p-4C_6H_4X-H_2P, as well as meta- and ortho- isomers (m-4C_6H_4X-H_2P and o-4C_6H_4X-H_2P) were compared. The results of the model studies demonstrate that the bond distances can be reliably determined from experimental data, while the refinement of the positions of halogenophenyl substituents relative to the macrocyclic core is at the limit of the possibilities of the GED method. Meta- and ortho- isomers of 4C_6H_4X-H_2P can be distinguished based on the experimental data, especially in the case of bromine-substituted phenyl groups.

Key words: quantum chemical calculations, DFT, porphyrin, conformational analysis

INTRODUCTION

According to modern concepts, the understanding of electronic and geometry structure of a molecule is the key point in interpretation and prediction of chemical, physical and biological properties of a compound. The structural studies commonly exploit a number of theoretical (quantum-chemical) and experimental (X-ray diffraction, gas-phase electron diffraction, etc.) methods. It should, however, be mentioned that the solid state structures determined by X-ray diffraction are usually distorted due to intermolecular interactions. Gas-phase structures do not suffer from these interactions and reflect the properties of a free molecule. The most common experimental method for structural determination of free molecules is the gas-phase electron diffraction (GED). The structures determined by GED can be used for the development of corresponding subsections of stereochemistry and for the assessment of performance of various theoretical methods. However, in the case of large molecules the structural refinement of GED data is usually a nontrivial procedure [1]. In particular, macroheterocyclic ligands and their metal complexes are characterized by a low volatility and require very high temperatures during effusion experiments [2]. The macroheterocyclic compounds can exhibit different types of non-planar distortions depending on the nature of central metal atom and kind of substituent [3-5], and this circumstance brings the additional difficulties in the structural analysis. Therefore, only few structures of macroheterocycles have been determined experimentally so far, while most studies of the free molecules of porphyrin derivatives were limited to quantum-chemical calculations.

In the literature one can find a series of GED investigations of the structures of phthalocyanine complexes [6-12]. However, among the porphyrins, only copper and tin octamethylporphyrins [13, 14] and copper and zinc etioporphyrins-II [15, 16] were studied by GED. The sensitivity of the GED method to the determination of the conformational composition of macrocyclic compounds bearing hydrocarbonic substutuents was examined and the refinement procedure was adjusted in [15, 16]. In the case of the metal etioporphyrins-II [15, 16] only the geometry of the macrocyclic framework, but not the relative positions of the $–CH_3$ and $–C_2H_5$ substituents can be reliably determined.

The present contribution continues the series of studies devoted to determination of sensitivity of GED method to the determination of conformational composition of macrocycles, but deals with substituents containing halogen atoms. The objects of study are 5,10,15,20-tetrakis(4’-halogenophenyl) porphyrin (p-$4C_6H_4X$-H_2P; X=F, Br).

The structures and the conformational diversity were examined with use of quantum-chemical calculations. Theoretical consideration of the sensitivity of GED method to the determination of conformational and isomeric composition of the vapor was also performed. For this purpose, *meta*- and *ortho*-isomers were also calculated: 5,10,15,20-tetrakis(3’-halogenophenyl)porphyrin (m-$4C_6H_4X$-H_2P; X=F, Br) and 5,10,15,20-tetrakis(2’-halogenophenyl) porphyrin (o-$4C_6H_4X$-H_2P; X=F, Br).

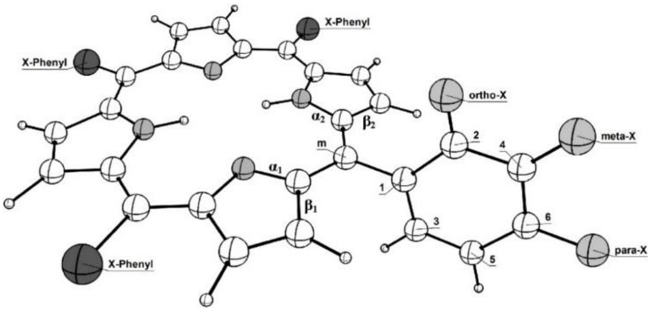

Fig. 1. Molecular structure and atom numbering of o-$4C_6H_4X$-H_2P, m-$4C_6H_4X$-H_2P, p-$4C_6H_4X$-H_2P (X=F, Br)
Рис. 1. Молекулярная структура и нумерация атомов для o-$4C_6H_4X$-H_2P, $м$-$4C_6H_4X$-H_2P, $п$-$4C_6H_4X$-H_2P (X=F, Br)

COMPUTATIONAL DETAILS

Structural parameters of p-$4C_6H_4X$-H_2P (X = F, Br) were optimized under C_{2V}, C_{2h} (two variants), D_2 and D_{2h} (two variants) symmetries, under C_2, D_2, C_1, C_{2h} (two variants) and C_{2v} symmetries – for m-$4C_6H_4X$-H_2P (X = F, Br) and under D_2, C_1, C_{2h} (two variants) and C_{2v} symmetries – for o-$4C_6H_4X$-H_2P (X = F, Br). Vibrational frequencies were calculated for all the optimized structures. All calculations were performed using DFT (B3LYP functional [17,18]). In order to examine the influence of basis set on relative energies and structural parameters, five basis sets were tested in the case of p-$4C_6H_4F$-H_2P:(A) 6-31G(d,p)[19]; (B) pVTZ, taken from the EMSL library [20] (denoted as «*GAMESSpVTZ*»); (C) cc-pVTZ [21]; (D) pcseg-2 [22]. Basis set (B) was chosen for the calculations of $4C_6H_4Br$-H_2P. Core electrons of Br atom were described by pseudopotential ECP10MDF [23] and the valence shell was described by cc-pVTZ-PP (10s11p9d1f)/[5s4p3d1f] basis set [23]. The calculations were carried out utilizing Gaussian 03 program package. The optimized structures from quantum chemical calculations at B3LYP/(B) level are given in Supplementary material [http://journals.isuct.ru/ctj/article/view/1799].

RESULTS AND DISCUSSION

According to the results of calculations, four optimized structures (conformers p-I – p-IV, see Fig. 2) of p-$4C_6H_4X$-H_2P correspond to minima on the potential energy surface. Conformer I possesses the lowest energy (see Table 1), however the energies of conformers p-II – p-IV are only slightly higher. Conformation p-V corresponds to the saddle point of 4th order on the PES with imaginary frequencies describing rotation of the groups $–C_6H_4X$. Conformation p-VI also corresponds to the saddle point. The imaginary frequencies describe rotation of the substituents and out-of-plane distortions of macrocycle.

Note, that the different basis sets give the same qualitative picture of the relative energies of considered structures (Table 1). The molecular parameters of similar type calculated with use of the basis sets A–D possess close values. The maximum deviation of the bond length is 0.008 Å that is close to the typical uncertainty of GED experiment. It should be mentioned that the use of basis sets C-D requires much more computational time as compared to A–B (Table 1). Therefore, the calculations of $4C_6H_4Br$-H_2P were only performed with use of basis set pVTZ (B).

Conformational analysis for *ortho*- and *meta*-isomers of $4C_6H_4X$-H_2P was performed in the similar way as in our previous study of metal etioporphyrin-II [15,16]. Models I-V (Fig. 3) differ in the orientation of the halogen atom relative to the macrocyclic fragment. According to the results of calculations, the conformers m-I(I) and o-I possess the lowest energies (Table 3) for m-$4C_6H_4X$-H_2P and p-$4C_6H_4X$-H_2P, respectively.

Comparison of molecular parameters of similar type for *p*-$4C_6H_4F$-H_2P and *p*-$4C_6H_4Br$-H_2P (Table 4) leads to conclusion that the nature of a halogen does not influence significantly the structure of entire molecule. Elongation of the bond C–X by ~0.6 Å in the Br-substituted molecule does not lead to noticeable deformations of macrocycle and, therefore, does practically not influence the relative energies of the conformers.

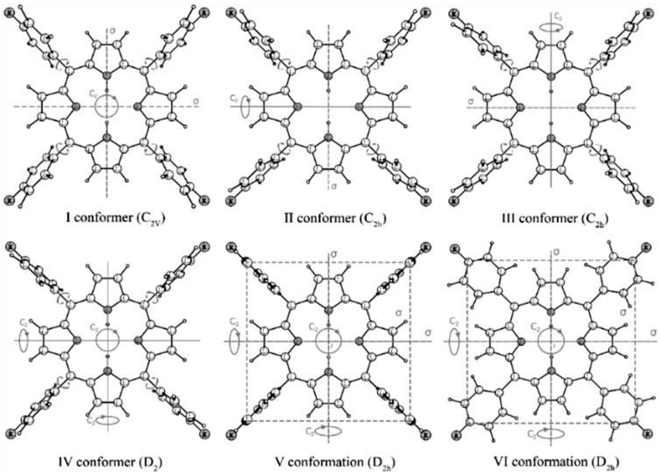

Fig. 2. Conformer models of *p*-$4C_6H_4X$-H_2P
Рис. 2. Модели конформеров *п*-$4C_6H_4X$-H_2P

Table 1

Relative energies of conformers p-I – p-IV, conformations of p-V – p-VI of *p*-$4C_6H_4X$-H_2P, where X=F, Br, and relative CPU time for single point calculations with use of the different basis sets

Таблица 1. **Относительные энергии конформеров p-I – p-IV, конформаций p-V – p-VI *п*-$4C_6H_4X$-H_2P, где X=F, Br, и относительное время расчетов с использованием различных наборов базисных функций**

	Structure	p-I	p-II	p-III	p-IV	p-V	p-VI	Rel. time [a]
X	Symmetry	C_{2v}	C_{2h}	C_{2h}	D_2	D_{2h}	D_{2h}	C_{2v}
F	ΔE, $kJmol^{-1}$(A)[b]	0.00	1.15	1.30	2.51	5.02	769.37	1.0
	ΔE, $kJmol^{-1}$(B)[b]	0.00	0.43	0.50	0.86	0.99	767.43	6.1
	ΔE, $kJmol^{-1}$(C)[b]	0.00	0.26	0.62	1.08	1.31	754.75	16.7
	ΔE, $kJmol^{-1}$(D)[b]	0.00	0.47	0.53	0.94	1.12	757.86	34.7
Br	ΔE, $kJmol^{-1}$(B)[b]	0.00	0.42	0.50	0.91	1.10	760.45	-

Notes: a The ratio of CPU time of 5 cycles of SCF procedure within a single point calculation at different theory levels to 5 cycles of a single point CPU time of calculations using basis set (A); b (A), (B), (C), (D) basis sets are described in Computational details

Примечания: a относительное компьютерное время, затраченное на 5 SCF-итераций «Single point» расчета;b наборы базисных функции (A), (B), (C), (D) описаны в разделе Computational details

Table 2

Molecular parameters (internuclear distances, Å; angles, °) of conformer p-I of *p*-$4C_6H_4F$-H_2P calculated with use of the different basis sets

Таблица 2. **Молекулярные параметры (межъядерные расстояния, Å; углы, °) *п*-$4C_6H_4F$-H_2P (конформер p-I), рассчитанные с использованием различных базисных наборов**

	B3LYP/basis sets			
Parameter	(A)	(B)	(C)	(D)
N_i-$C_{\alpha\,(1)}$	1.367	1.364	1.362	1.361
C_α-$C_{\beta\,(1)}$	1.460	1.458	1.456	1.456
C_β-$C_{\beta\,(1)}$	1.354	1.351	1.348	1.349
C_m-$C_{\alpha\,(1)}$	1.412	1.408	1.406	1.406
C_m-$C_{\alpha\,(2)}$	1.406	1.401	1.399	1.399
N_i-$H_{i\,(2)}$	1.014	1.011	1.010	1.010
N_i-$C_{\alpha\,(2)}$	1.376	1.374	1.372	1.372
C_α-$C_{\beta\,(2)}$	1.434	1.432	1.430	1.430
C_β-$C_{\beta\,(2)}$	1.369	1.367	1.364	1.364
C_m-C_1	1.497	1.499	1.496	1.497
C_1-C_2	1.404	1.399	1.397	1.397
C_1-C_3	1.405	1.399	1.397	1.397
C_2-C_4	1.394	1.392	1.390	1.390
C_3-C_5	1.394	1.392	1.389	1.390
C_4-C_6	1.390	1.385	1.383	1.383
C_5-C_6	1.390	1.385	1.383	1.383
C-F	1.349	1.355	1.349	1.351
$C_{\alpha(2)}$-C_m-C_1-C_2	65.3	72.9	71.9	72.4
N_i-C_α-$C_{\beta\,(1)}$	110.9	110.7	110.7	110.6
C_α-C_β-$C_{\beta\,(1)}$	106.3	106.4	106.4	106.4
C_α-C_m-C_α	125.2	125.4	125.3	125.4
N_i-C_α-$C_{\beta\,(2)}$	106.5	106.4	106.4	106.4
C_α-C_β-$C_{\beta\,(2)}$	108.2	108.2	108.2	108.2

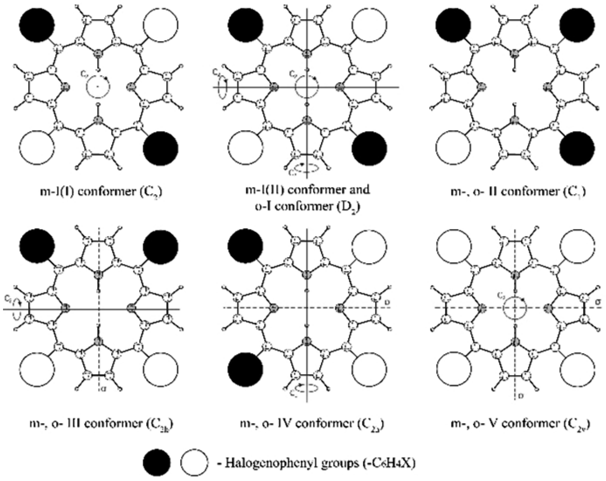

Fig. 3. Conformer models of *m*-$4C_6H_4X$-H_2P, *o*-$4C_6H_4X$-H_2P. Top view: the orientation of the X-atom (X=F, Br) with respect to the plane of the porphyrin macrocycle: (black)—above the plane, (white)—below the plane

Рис. 3. Модели конформеров *м*-$4C_6H_4X$-H_2P и *о*-$4C_6H_4X$-H_2P. Вид сверху показывает ориентацию атомов X (X=F, Br) относительно плоскости порфиринового макроцикла: (черный) – над плоскостью, (белый) – под плоскостью

Table 3

Relative energies of conformers of *m*-4C_6H_4X-H_2P and *o*-4C_6H_4X-H_2P, where X=F, Br

Таблица 3. **Относительные энергии конформеров *м*-4C_6H_4X-H_2P и *о*-4C_6H_4X-H_2P, где X=F, Br**

X	*m*- isomer	m-I(I)	m-I(II)	m-II	m-III	m-IV	m-V
	symmetry	C_2	D_2	C_1	C_{2h}	C_{2h}	C_{2v}
F	ΔE, kJmol^{-1}(B)^a	0.00	0.67	0.21	0.40	0.58	0.40
Br	ΔE, kJmol^{-1}(B)^a	0.00	0.57	0.17	0.36	0.56	0.36
X	*o*- isomer	o-I		o-II	o-III	o-IV	o-V
	symmetry	D_2		C_1	C_{2h}	C_{2h}	C_{2v}
F	ΔE, kJmol^{-1}(B)^a	0.00		0.71	0.50	0.53	1.65
Br	ΔE, kJmol^{-1}(B)^a	0.00		0.76	0.65	0.73	1.68

Note: a (B) basis sets are described in Computational details
Примечание: a базисные функции (B) описаны в разделе Computational details

Analysis of the sensitivity of the GED method to the determination of the conformational and isomeric composition of the 4C_6H_4X-H_2P (X=F, Br) vapor

In order to assess the ability of GED method to distinguish between conformations of *p*-4C_6H_4X-H_2P molecule, a series of calculations of the model radial distributions curves f(r) was performed using results of B3LYP/(B) calculations. Vibrational amplitudes and corrections to the internuclear distances at the estimated temperature of GED experiment of T = 600 K were calculated with the use of VibModule program [24] (second approximation) on the basis of the force field obtained from quantum chemical calculations at B3LYP/(B) level.

Table 4

Comparison of structural parameters (internuclear distances, Å; angles, °) for 4C_6H_4X-H_2P (*p*-, *m*-, *o*- isomers, X=F, Br) from B3LYP/(B) calculations

Таблица 4. **Структурные параметры (межъядерные расстояния, Å; углы, °) 4C_6H_4X-H_2P (*п*-, *м*-, *о*- изомеры), где X=F, Br, согласно расчетам B3LYP/(B)**

Parameter	X=F(p-I conf) *p*-isomer	X=Br(p-Iconf.) *p*-isomer	X=F (C_2) *m*-isomer	X=Br (C_2) *m*-isomer	X=F (D_2) *o*-isomer	X=Br (D_2) *o*-isomer
N_i-$C_{\alpha\,(1)}$	1.364	1.364	1.364	1.364	1.363	1.363
C_α-$C_{\beta\,(1)}$	1.458	1.458	1.458	1.458	1.458	1.458
C_β-$C_{\beta\,(1)}$	1.351	1.351	1.351	1.351	1.351	1.351
C_m-$C_{\alpha\,(1)}$	1.408	1.408	1.408	1.408	1.406	1.406
C_m-$C_{\alpha\,(2)}$	1.401	1.401	1.401	1.401	1.399	1.399
N_i-$H_{i\,(2)}$	1.011	1.011	1.011	1.011	1.011	1.011
N_i-$C_{\alpha\,(2)}$	1.374	1.374	1.374	1.374	1.373	1.373
C_α-$C_{\beta\,(2)}$	1.432	1.432	1.432	1.432	1.432	1.432
C_β-$C_{\beta\,(2)}$	1.367	1.367	1.366	1.366	1.366	1.366
C_m-C_1	1.499	1.498	1.499	1.499	1.499	1.500
C_1-C_2	1.399	1.399	1.399	1.398	1.400	1.401
C_1-C_3	1.399	1.399	1.399	1.399	1.393	1.400
C_2-C_4	1.392	1.393	1.392	1.392	1.392	1.390
C_3-C_5	1.392	1.392	1.385	1.390	1.387	1.393
C_4-C_6	1.385	1.390	1.393	1.393	1.393	1.392
C_5-C_6	1.385	1.390	1.385	1.390	1.391	1.391
C-X	1.355	1.913	1.356	1.915	1.354	1.916
$C_{\alpha 2}$-C_m-C_1-C_2	72.9	72.5	73.8	74.2	86.3	89.9
N_i-C_α-$C_{\beta\,(1)}$	110.7	110.7	110.8	110.8	110.8	110.8
C_α-C_β-$C_{\beta\,(1)}$	106.4	106.4	106.4	106.4	106.4	106.4
C_α-C_m-C_α	125.4	125.4	125.5	125.6	125.7	125.7
N_i-C_α-$C_{\beta\,(2)}$	106.4	106.4	106.5	106.5	106.5	106.5
C_α-C_β-$C_{\beta\,(2)}$	108.2	108.2	108.2	108.2	108.1	108.1

The results of the calculations are shown on Fig. 4 and 5 (note, that the difference curves Δf(r) were calculated relative to 1st curve corresponding to conformer p-I of *p*-4C_6H_4X-H_2P: $\Delta f(r) = f_j(r) - f_1(r)$).

The deviation of *j*-th curve from 1st curve was characterized by disagreement factor:

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

between the theoretical molecular scattering intensities corresponding to different models ($R_{f,j}$ is disagreement factor; $sM(s_i)_{model\,1}$ – theoretical molecular scattering intensities for conformer p-I; $sM(s_i)_{model\,j}$ – theoretical molecular scattering intensities for corresponding conformer or isomer). The difference between f(r) curves in the case of *p*-$4C_6H_4F$-H_2P (in the ranges ~3.1-3.6 Å and ~4.4-4.8 Å) molecule is caused by change of distances $C_{Ph}\ldots C_{Porph}$ due to different orientation of the halogenophenyl groups relative to the porphyrin core: the torsional angles $\tau(C_{\alpha 2}$-C_m-C_1-$C_2)$ are: 72.9^0 (p-I) and 81.3^0 (p-IV); 72.5^0 (p-I) and 80.1^0 (p-IV) for $4C_6H_4F$-H_2P and $4C_6H_4Br$-H_2P, respectively. The analogous study for copper and zinc etioporphyrins-II [15,16] yielded the values of $R_f \leq 1.1\%$ with the values of relative energies between the conformers being as low as ~0.3 kJ mol^{-1}.

An attempt to distinguish between the isomers of $4C_6H_4X$-H_2P (*ortho*-, *meta*-, *para*-) was also made.

According to the difference curves Δf(r), the *ortho*- and *meta*-isomers of $4C_6H_4X$-H_2P can be quite well distinguished from the most energetically favorable *para*-isomer. The differences are caused by significant changes in the distances between non-bonded atoms X…X, N…X, C…X and C…C. The bond lengths in the porphyrin core and phenyl rings are almost the same in the *para*-, *ortho*- and *meta*-isomers (see Table 4). Note, that the differences in f(r) between the isomers are much more pronounced in the case of $4C_6H_4Br$-H_2P due to higher scattering ability of the Br atom as compared to F.

According to the results of theoretical modeling performed in the present study, bond lengths and bond angles in the macrocyclic core and halogen-substituted phenyl rings are almost the same values in all conformers of *p*-$4C_6H_4X$-H_2P considered. However, the changes in the distances between non-bonded atoms influence the model molecular intensities *s*M(*s*) and therefore an attempt can be made to distinguish between the conformers based on the experimental GED data. It should be noted that this problem is at the limit of the possibilities of GED method and only the effective position of halogenophenyl groups are apparently refinable. At the same time, bond lengths and bond angles can be refined with a typical accuracy of GED method. Therefore, the geometry structures of macrocyclic core and halogenophenyl rings can be reliable determined.

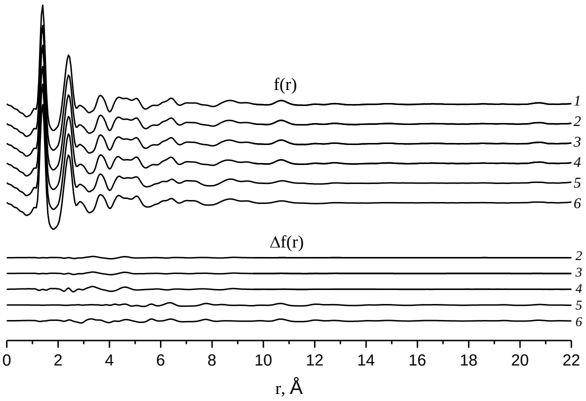

Fig. 4. Comparison of theoretical radial distribution functions f(r) of $4C_6H_4F$-H_2P models: 1 - conformer p-I, 2 - conformer p-II, 3 – conformer p-III, 4 - conformer p-IV, 5 - m-I(I) conformer of *m*-isomer, 6 - o-I conformer of *o*-isomer; comparison of differences functions Δf(r) concerning 1: 2 - conformer p-II (R_f =2.36 %), 3 – conformer p-III (R_f =2.75 %), p-4 - conformer IV (R_f = 5.08 %), 5 - m-I(I) conformer of *m*-isomer (R_f =4.98 %), 6 - o-I conformer of *o*-isomer (R_f =5.86 %). Molecular parameters were calculated at B3LYP/(B) theory level

Рис. 4. Сравнение теоретических функций радиального распределения f(r) для $4C_6H_4F$-H_2P: 1 - конформер p-I, 2 - конформер p-II, 3 - конформер p-III, 4 - конформер p-IV, 5 – m-I(I) конформер *м*-изомера, 6 – o-I конформер *о*-изомера; разностных функций Δf(r), рассчитаны относительно 1: 2 - конформер p-II (R_f =2,36 %), 3 - конформер p-III (R_f =2,75 %), 4 - конформер p-IV (R_f =5,08 %), 5 - m-I(I) конформер *м*-изомера C2 (R_f =4,98 %), 6 - o-I конформер *о*-изомера (R_f =5,86 %). Молекулярные параметры рассчитаны в приближении B3LYP/(B)

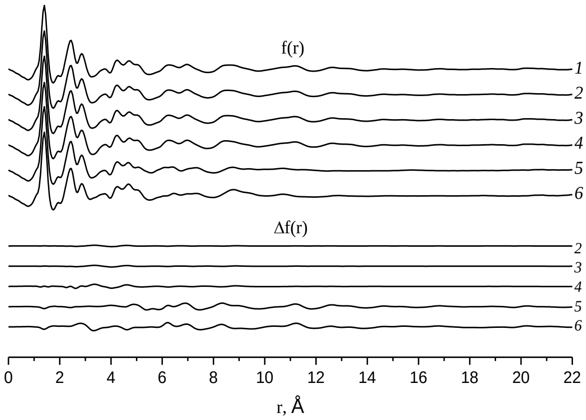

Fig. 5. Comparison of theoretical radial distribution functions f(r) of $4C_6H_4Br$-H_2P models: 1 - conformer p-I, 2 - conformer p-II, 3 - conformer p-III, 4 - conformer p-IV, 5 - m-I(I) conformer of *m*-isomer, 6 - o-I conformer of *o*-isomer; comparison of differences functions Δf(r) concerning 1: 2 - conformer p-II (R_f =2.15 %), 3 - conformer p-III (R_f =2.51 %), 4 - conformer p-IV (R_f =6.09 %), 5 - m-I(I) conformer of *m*-isomer (R_f =17.33 %), 6 - o-I conformer of *o*-isomer (R_f =18.50 %). Molecular parameters were calculated at B3LYP/(B) theory level

Рис. 5. Сравнение теоретических функций радиального распределения f(r) для $4C_6H_4Br$-H_2P: 1 - конформер p-I, 2 - конформер p-II, 3 - конформер p-III, 4 - конформер p-IV, 5 - m-I(I) конформер *м*-изомера, 6 - o-I конформер *о*-изомера; разностных функций Δf(r), рассчитаны относительно 1: 2 - конформер p-II (R_f =2,15 %), 3 - конформер p-III (R_f =2,51 %), 4 - конформер p-IV (R_f =6,09 %), 5 - m-I(I) конформер *м*-изомера (R_f =17,33 %), 6 - o-I конформер *о*-изомера (R_f =18,50 %). Молекулярные параметры рассчитаны в приближении B3LYP/(B)

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