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PII: S0040-4020(19)30082-1

DOI: https://doi.org/10.1016/j.tet.2019.01.043

Reference: TET 30095

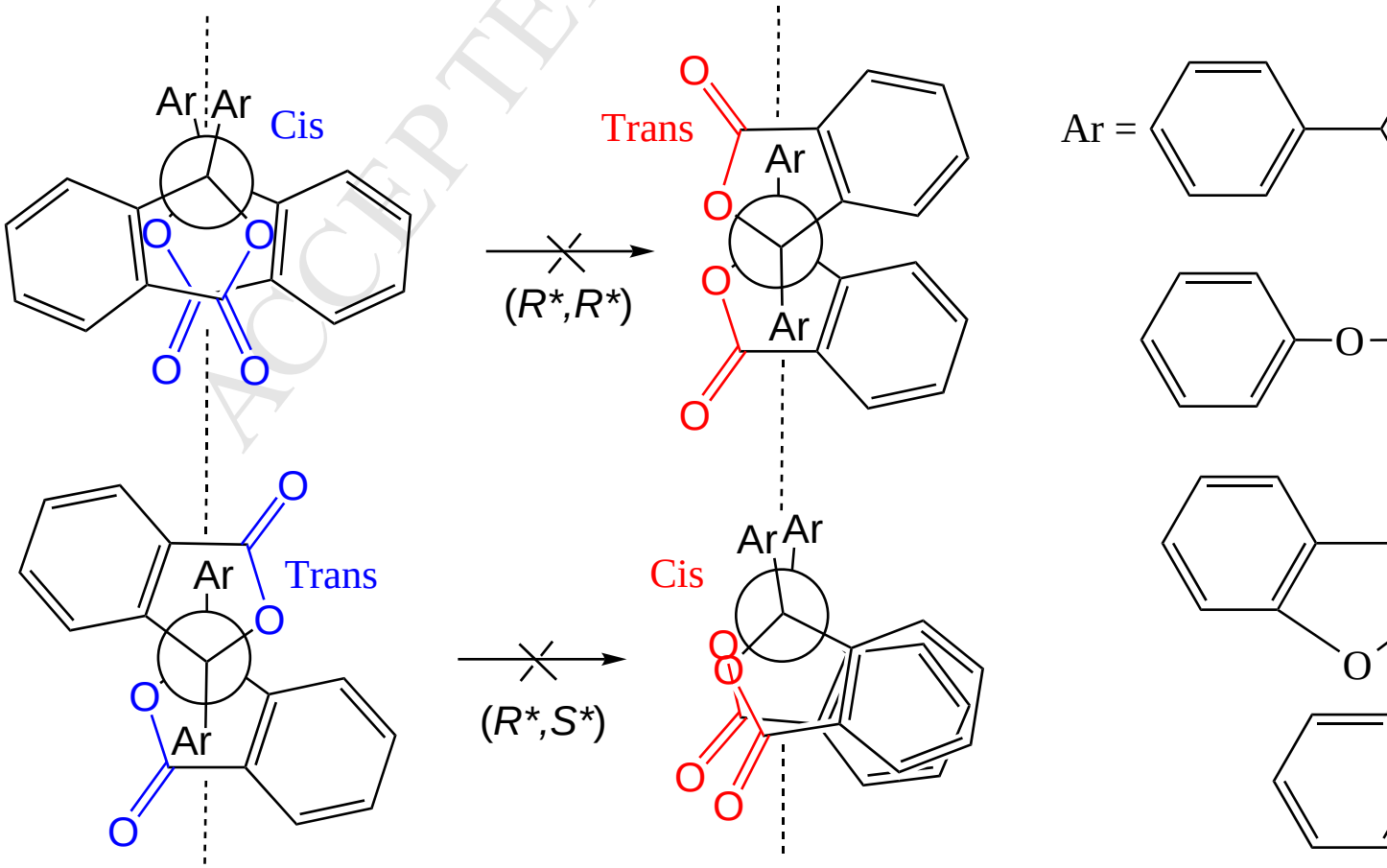
To appear in: *Tetrahedron*

Received Date: 28 November 2018

Revised Date: 16 January 2019

Accepted Date: 17 January 2019

Please cite this article as: Yangirov TA, Fatykhov AA, Sedova EA, Khalilov LM, Meshcheryakova ES, Ivanov SP, Salazkin SN, Kraikin VA, The rotameric (*R*,S**)- and (*R*,R**)-biaryl-3,3′-diphthalides of polyphenylene series, *Tetrahedron* (2019), doi: https://doi.org/10.1016/j.tet.2019.01.043.

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# The rotameric (*R*,S**)- and (*R*,R**)-biaryl-3,3′-diphthalides of polyphenylene series

Tagir A. Yangirov[a], Akhnef A. Fatykhov[a], Elvira A. Sedova[a], Leonard M. Khalilov[b], Ekaterina S. Meshcheryakova[b], Sergey P. Ivanov[a], Sergey N. Salazkin[c], Vladimir A. Kraikin[a,*]

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ABSTRACT

A wide range of diastereomeric pairs of biaryl-3,3′-diphthalides with aromatic (heteroaromatic) substituents of polyphenylene series (including halogen substituted) was synthesized. All of them were separated and characterized by the methods of X-ray analysis, HPLC, IR-, 1H and 13C NMR spectroscopy. It was determined that solubility, tendency to adsorption and related to it retention times, chemical shifts of equivalent hydrogen and carbon atoms of biaryl-3,3′-diphthalides diastereoisomers are determined firstly by the stereo-electronic effects of two adjacent strongly polar phthalide groups. It was shown that both in crystalline phase and in solution all the diphthalides, regardless of the chemical structure of their substituents, are existing as stable rotamers with ***cis*** or synperiplanar (chiral forms) and ***trans*** or antiperiplanar (*meso*-forms) conformation.

*Key words:* biaryl-3,3′-diphthalides, *meso*- and chiral diastereomers, ***cis*** and ***trans*** rotamers, X-ray analysis, 1H and 13C NMR.

## Introduction

The compounds of the class of diphthalides have been known for more than 120 years starting with the work of Ulman[1], who first obtained biphenyl-3,3′-diphthalide. But despite of the long history, a relatively small number of diphthalides with mononuclear substitutes have been synthesized to date. Most of them are compounds obtained on

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the basis of commercially available and well soluble derivatives of *o*-benzoylbenzoic acid and its substituted analogs (*o*-(*p*-nitrobenzoyl)-benzoic, *o*-(*p*-methylbenzoyl)-benzoic etc.). Practically all ways of obtaining biphenyl-3,3′-diphthalides are based on the dimerization of intermediates (cation, radical) formed by heterolysis or homolysis of C–X bond, where C represents a $sp^3$-hybridised carbon atom of phthalide group, and X is a hydrogen atom or heteroatom O, S, N, Cl. The pioneering biaryl-3,3′-diphthalides were produced by the reduction of benzoylbenzoic acids and their esters by various metals in the acidic media: Zn/acetic acid[2,3], Al/sulfuric acid[4,5]. Another early methods of synthesizing the diphthalides involve dimerization of 3-arylphthalides in the presence of the halogens $Br_2$[6] and $I_2$[7]. The well known Bhatt's method suggests the dimerization of benzoylbenzoic pseudoacid chlorides by treatment with sodium or potassium iodides[8,9]. Applying these reductants leads to 3,3′-diphthalides with high yields in mild conditions[8-10]. Later the diphthalides were obtained by carbonylation of β-iodoenones[11], photopinacolisation-lactonisation of *o*-benzoylbenzoic acid and photolysis of amides[12], as well by photoreduction of alkylbenzoates[13-15]. Also, the formation of biaryl-3,3′-diphthalides during the photochemical transformation of S-aryl 2-benzoylbenzothioates was described[16]. And just recently, there was a report dealing with the microwave assisted synthesis of 3-amine dithiocarbamyl phthalides and their further transformation to dihydro-3,3′-diphthalides[17].

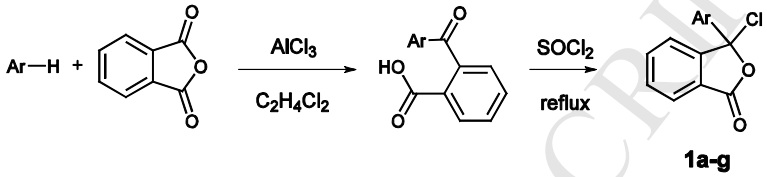
With all diversity of the synthetic methods, the structural investigations were performed just for a small amount of 3,3′-diphthalides. Using the X-ray analysis, the molecular structures of biphenyl-3,3′-diphthalide, bis-(4-chlorophenyl)-3,3′-diphthalide and bis-(4-bromophenyl)-3,3′-diphthalide were investigated[18-21]. It's shown that *meso*-forms of the diphthalides always exist in the staggered configuration, while there is no reliable information concerning configurational structure of the chiral isomers. Besides the X-ray analysis, nowadays there are no general physical methods for precise distinguishing between (*R*,S**)- and (*R*,R**)-isomers of diphthalides[18]. In the Pfau's work[12] the 13C NMR spectra of both isomers of biphenyl-3,3′-diphthalide are presented, however, without assignment of each spectrum to individual diastereomeric form.

The present report reveals the synthesis and the structure of 8 diastereomeric pairs of new biaryl-3,3′-diphthalides, with substituents of polyphenylene series, that we succeeded to separate, to characterize with various physical-chemical methods and to determine their relative configuration and the preferred conformation. The compounds of this type could find application as monomers for producing the polyheteroarylenes

with diphthalide groups in polymeric chain[22] by the reactions of dehalogenation[23-25] or Friedel-Crafts electrophilic substitution[26,27].

## Results and discussion

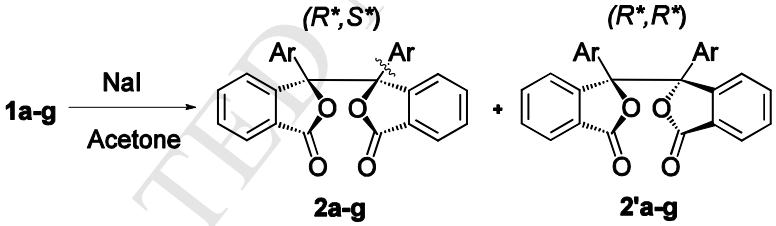
At first, the phthalic anhydride was condensed with commercially available aromatic (heteroaromatic) hydrocarbons by the Friedel-Crafts reaction to synthesize the starting *o*-aroylbenzoic acids that were transformed to corresponding pseudo acids chlorides **1a-g** by refluxing in thionyl chloride (Scheme 1).

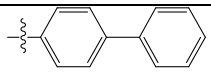
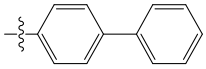
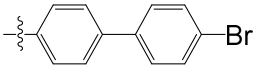
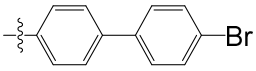
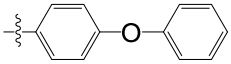
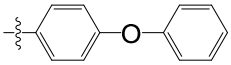
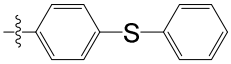


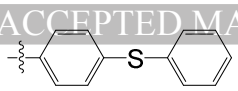
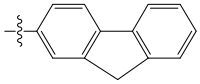
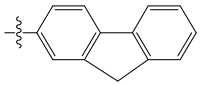
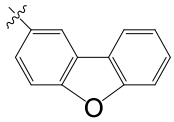
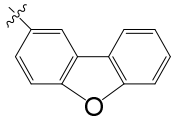
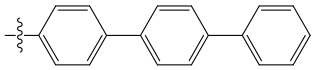
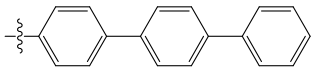

**Scheme 1.** Preparation of *o*-aroylbenzoic pseudo acids chlorides **1a-g**.

The further coupling of **1a-g** with NaI in acetone media at room temperature led to diastereoisomeric pairs of biaryl-3,3′-diphthalides **2a-g/2'a-g** which were not described before our investigations (Table 1).

**Table 1.** Synthesis of biaryl-3,3'-diphtalides **2a-g/2'a-g.**



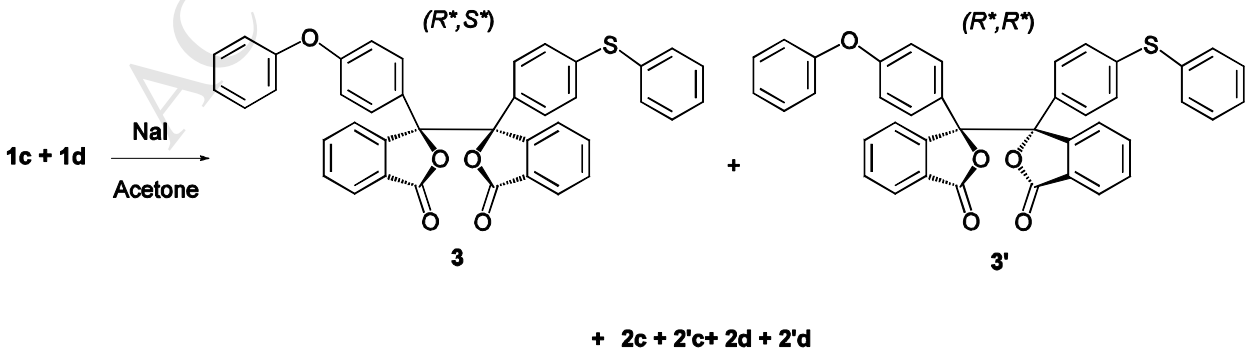

| Entry | Ar | Product | Form | Yield[a] (%) |
|---|---|---|---|---|
| 1 |  | **2a** | (*R**,*S**) | 97 |
| 2 |  | **2'a** | (*R**,*R**) | |
| 3 |  | **2b** | (*R**,*S**) | 80 |
| 4 |  | **2'b** | (*R**,*R**) | |
| 5 |  | **2c** | (*R**,*S**) | 80 |
| 6 |  | **2'c** | (*R**,*R**) | |
| 7 |  | **2d** | (*R**,*S**) | 95 |

| | | | | |
|---|---|---|---|---|
| 8 |  | **2'd** | (*R*,R**) | |
| 9 |  | **2e** | (*R*,S**) | 80 |
| 10 |  | **2'e** | (*R*,R**) | |
| 11 |  | **2f** | (*R*,S**) | |
| 12 |  | **2'f** | (*R*,R**) | 95 |
| 13 |  | **2g** | (*R*,S**) | |
| 14 |  | **2'g** | (*R*,R**) | 94 |

[a] General yield for both diastereomers. The molar ratio (*R*,S**)/ (*R*,R**) is 1:1.

In all cases the dimerization was followed by precipitation of the produced 3,3′-diphthalides, whereas the dimerization of poor soluble pseudo acids chlorides **1a-b, 1e-g** proceeded heterogeneously from the very beginning. Nevertheless, conducting the dehalogenation in heterophase conditions didn't affect the efficiency and selectivity of the process.

In addition to homo coupling of **1a-g**, in the present work we carried out the joint coupling of pseudo acids chlorides of diphenyloxide (**1c**) and diphenylsulphide (**1d**) type. Separation of the resulting mixture by HPLC gave the individual diphthalides **2c-d/2'c-d**, and moreover, the unsymmetrical diastereometric diphthalides **3** and **3'** were first isolated (Scheme 2).




**Scheme 2.** Joint dimerization of pseudo acids chlorides **1c** and **1d**.

The molar ratio of **2c, 2'c, 3**, **3', 2d**, **2'd** in the products mixture, according to the 13C NMR data, amounted to 1: 1: 2: 2: 1: 1 correspondingly.

The significant differences in solubility of (*R*,S**)- and (*R*,R**)-biaryl-3,3′-diphthalides (the chiral forms posses higher solubility) made it possible to separate most part of the synthesized diastereomeric pairs. *Meso*-isomers with conjugated polyphenylene substituents **2a**, **2b**, **2e**-**g**, which are characterized by extremely low solubility, were quite easily freed from corresponding racemates **2'a**, **2′b**, **2'e**-**g** by extracting the initial diastereomeric mixture with hot toluene. A diastereomeric pair of more soluble diphthalides with heteroaromatic substituent **2d/2'd** was split by fractional crystallization from toluene. For separating the diastereomers of diphenyloxide type **2c**/**2'c,** which crystallized out jointly from all the used solvents, as well as for isolating the unsymmetrical diphthalides **3** and **3'**, the semi-preparative HPLC was applied.

All the diastereoisomers were characterized by the methods of 1H, 13C NMR, IR- and mass-spectroscopy. The crystallized compounds were investigated by X-ray analysis (Figure 1).

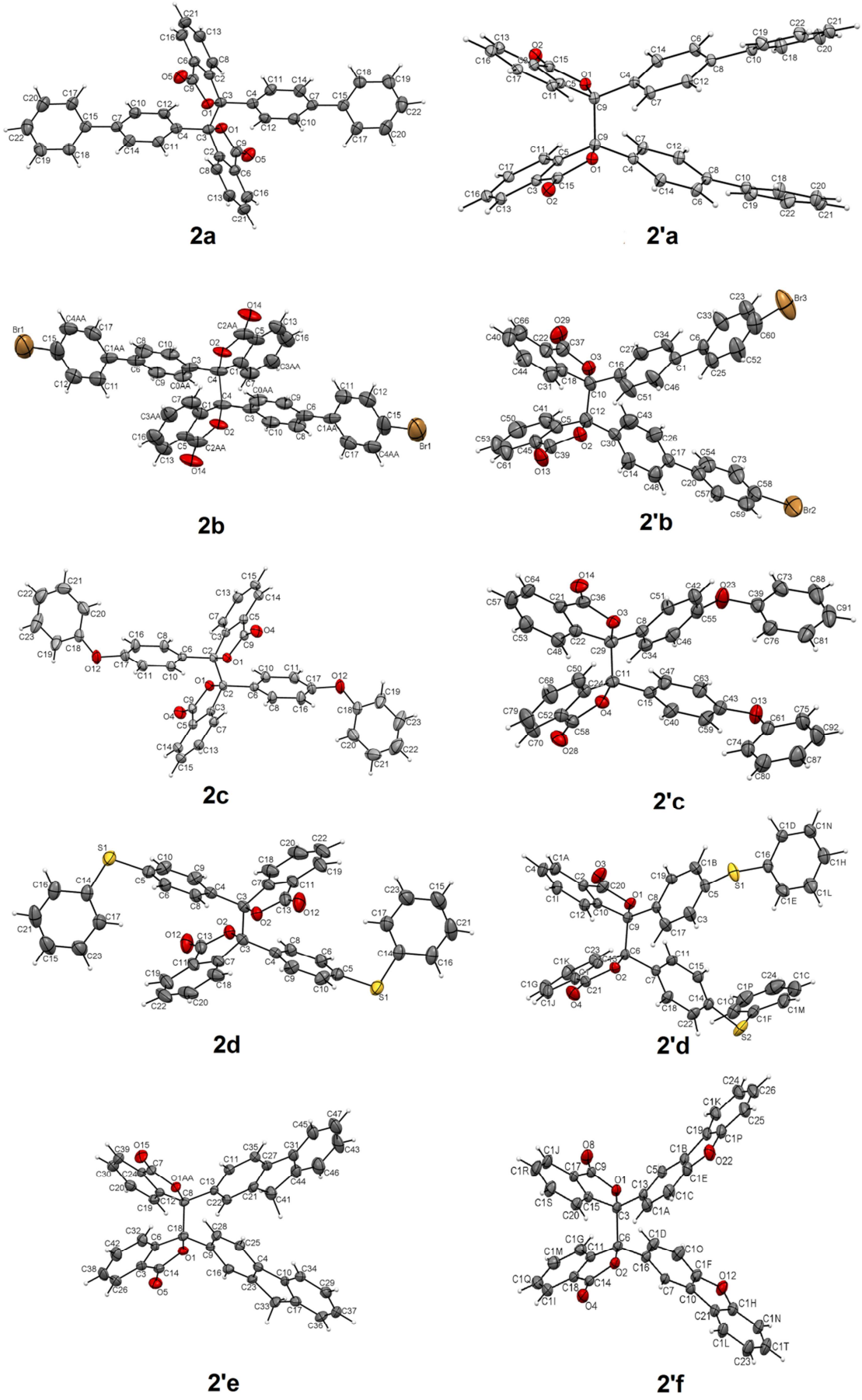



**Figure 1.** Molecular structures of biaryl-3,3′-diphthalides. Atoms are represented by thermal displacement ellipsoids at the 30% probability level.

In accordance with X-ray analysis data, all the investigated diphthalides, depending on their diastereomeric form, crystallize out as two stable conformers (rotamers) whose stability is determined by their configurational structure and by stereoelectronic effects of two adjacent strongly polar phthalide groups. The electrostatic repulsion of oxygen atoms (both ether and carbonyl) of phthalide groups and consequent retardation of C3–C3′ bond twisting lead to the fact that chiral diastereoisomers in crystalline phase exist in ***cis*** or synperiplanar conformation, and *meso*-isomers exist in ***trans*** or antiperiplanar one (Figure 2).

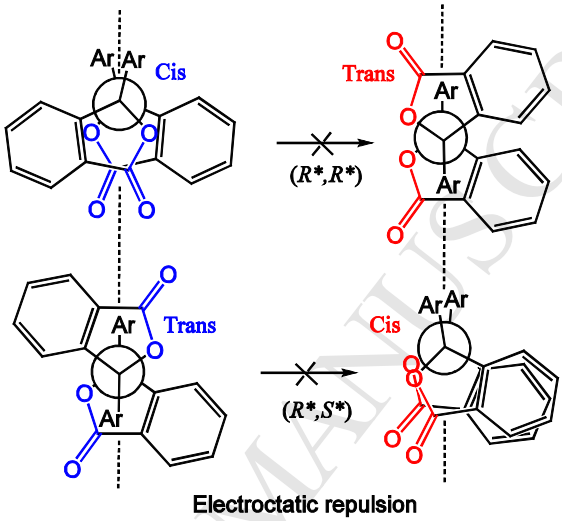



**Figure 2.** Favorable rotameric conformation of biaryl-3,3′-diphthalides diastereoisomers.

In both rotamers the electronegative oxygen atoms of adjacent phthalide groups keep away from each other at maximum. By the results of X-ray analysis, it was figured out that optimal value of a dihedral angle Ar–C3–C3′–Ar′ in (*R*,R**)-isomers amounts to the range from ~40° (**2'a**) to ~52° (**2'f**), and in *meso*-isomers always amounts to 180° (Table 2).

**Table 2.** Structural characteristics of biaryl-3,3'-diphtalides **2a-d/2'a-f** from the X-ray analyses data.

| Product | Unit cell | Space group | Angle[a] (°) |
|---|---|---|---|
| **2a** | orthorhombic | Pbca | 180.0 |
| **2'a** | tetragonal | $I4_1/a$ | 39.9 |
| **2b** | monoclinic | $P2_1/n$ | 180 |
| **2'b** | monoclinic | I2/a | 50.9 |
| **2c** | triclinic | P-1 | 180.0 |
| **2'c** | triclinic | P-1 | 43.5 |

| | | | |
|---|---|---|---|
| **2d** | triclinic | P-1 | 180.0 |
| **2'd** | monoclinic | $P2_1/n$ | 47.7 |
| **2e** | - | - | - |
| **2'e** | monoclinic | $P2_1/n$ | 42.4 |
| **2f** | - | - | - |
| **2'f** | triclinic | P-1 | 51.8 |

[a] Dihedral angle Ar-C3-C3′-Ar′

Most of obtained biaryl-3,3'-diphtalides form the crystal systems of triclinic (**2c**, **2'c**, **2d**, **2'f**) and monoclinic (**2'b, 2'd, 2'e)** syngony, diastereomer **2a** is of orthorhombic system and **2'a** is of tetragonal one. The diphthalide crystals of monoclinic crystallographic system posses a platy structure. This fact was confirmed on the example of **2'd** compound in which a classical image of a plastic slip deformation typical for the plate-like crystals was observed in polarized light (Figure 3).

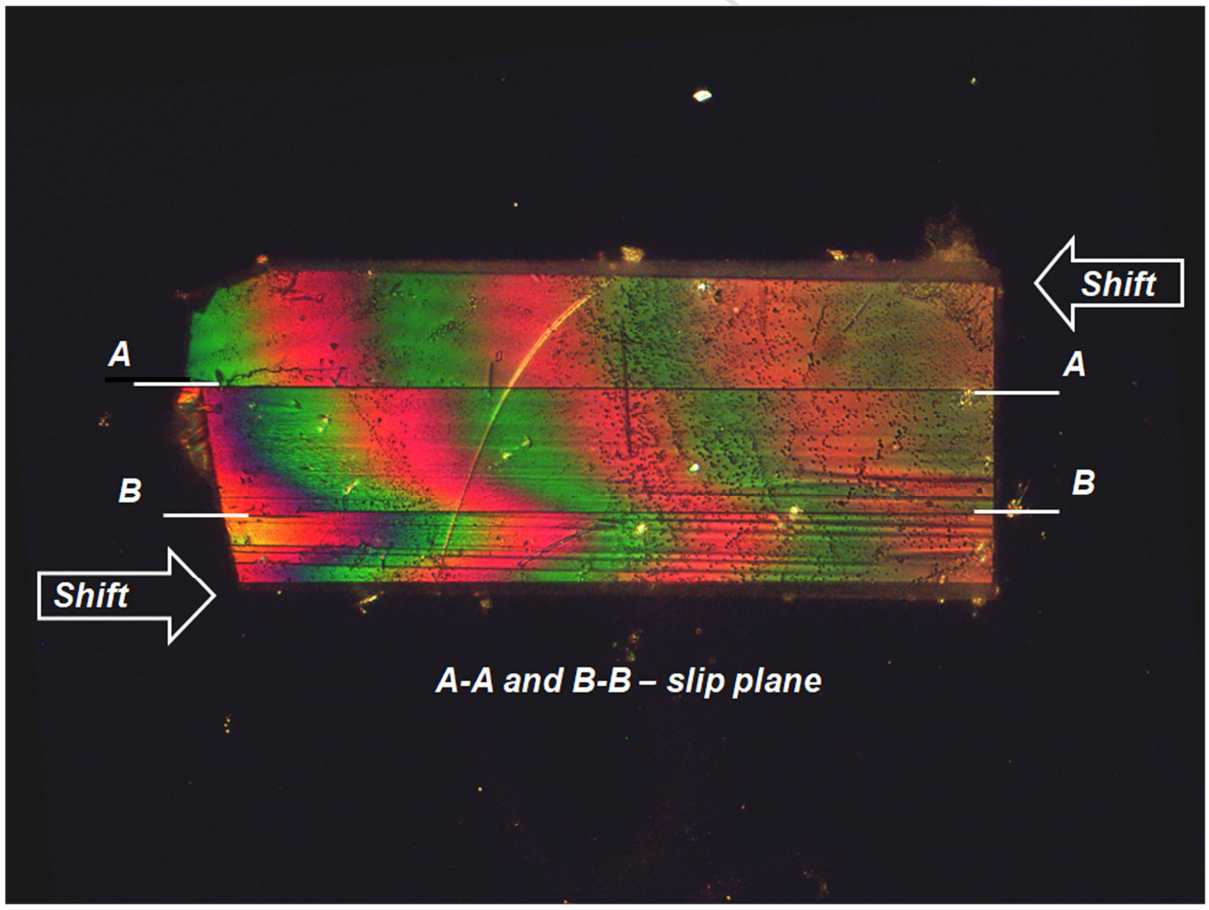
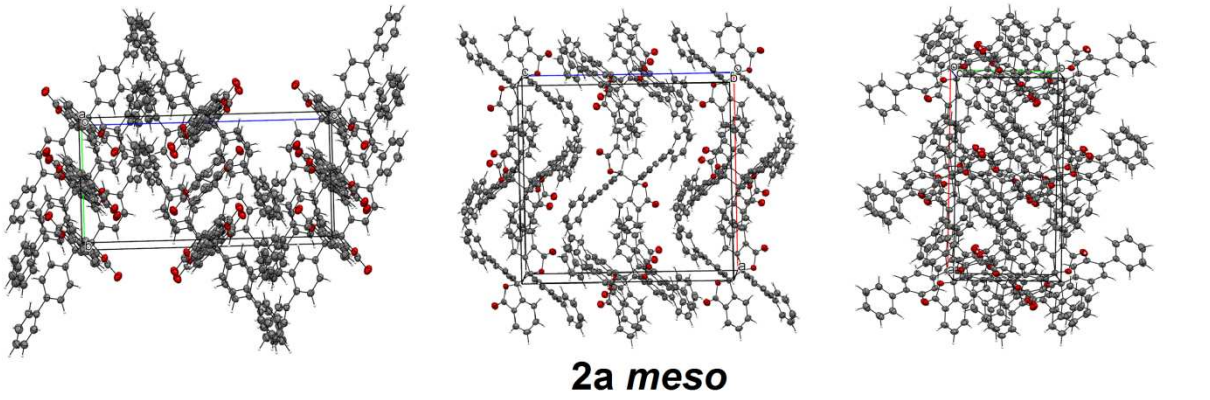
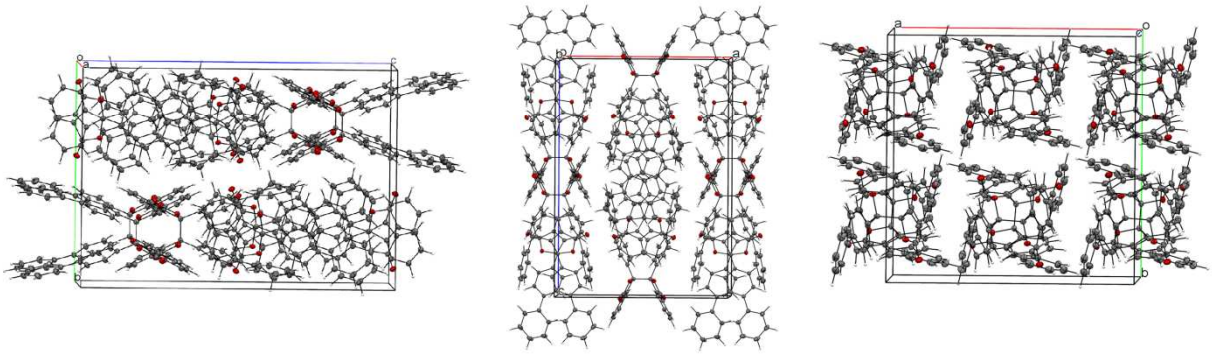



**Figure 3.** Plastic deformation of a platy crystal of (*R*,R**)-3,3'-bis[4-(phenylthio)phenyl]-3,3'-diphthalide observed in polarized light.

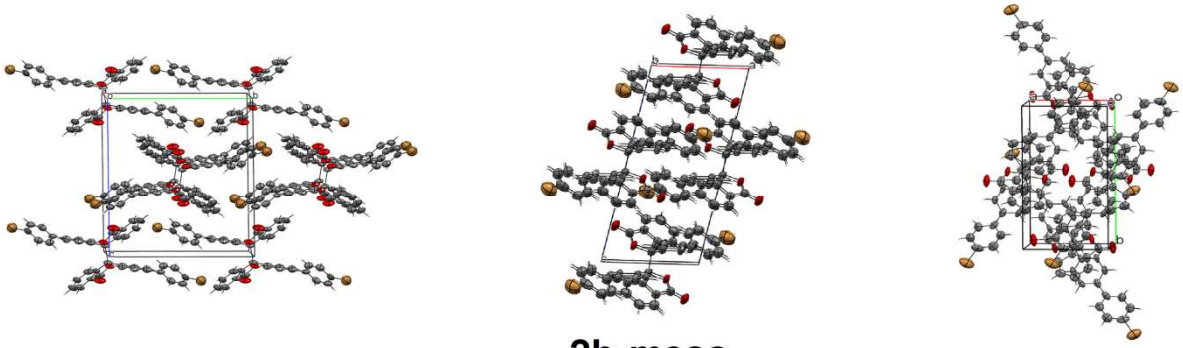
In Figure 4, which displays a molecular packing of (*R*,S**)- and (*R*,R**)-diastereomers of biaryl-3,3′-diphthalides **2a-d/2'a-d** along the crystallographic axes, one can see that formation of the crystals occurs via stacking-interaction.



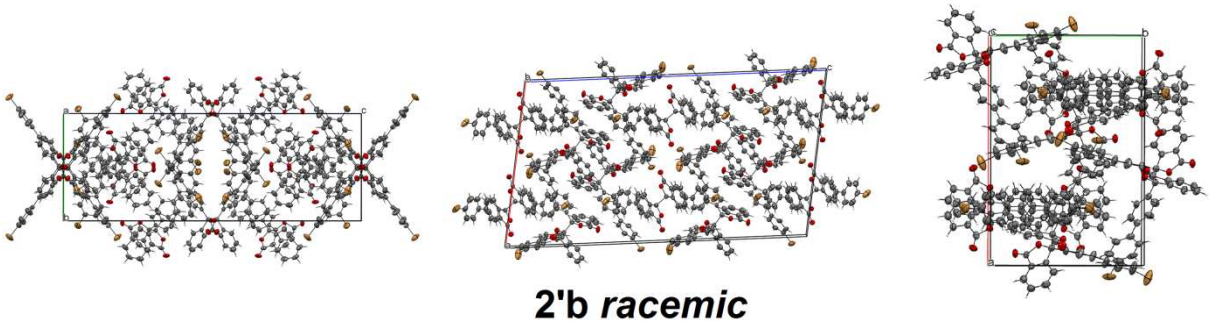
**2a *meso***



**2'a *racemic***



**2b *meso***



**2'b *racemic***

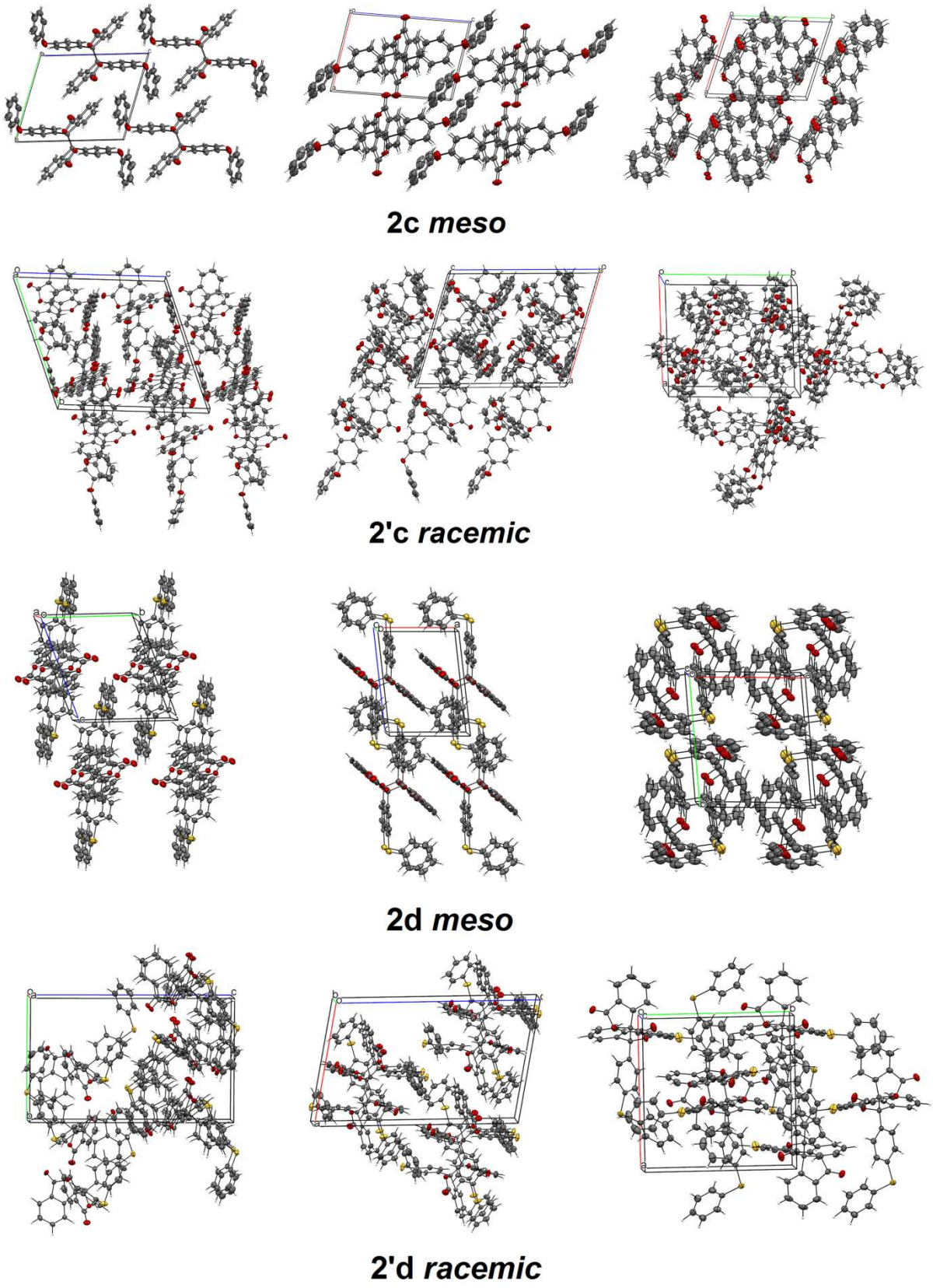



**Figure 4.** Molecular packing along the crystallographic axes for (*R*,S**)- and (*R*,R**)-biaryl-3,3'-diphthalide crystals **2a/2'a, 2b/2'b, 2c/2'c** and **2d/2'd.**

Cisoid form of (*R*,R**)-diastereomers and transoid form of (*R*,S**)-diastereomers of biaryl-3,3'-diphthalides keep up in a solution as well. This conclusion was made on the basis of HPLC data, according to which the *meso*-isomers are characterized by smaller retention times and always eluted first, and chiral diphthalides eluted second (Figure 5).

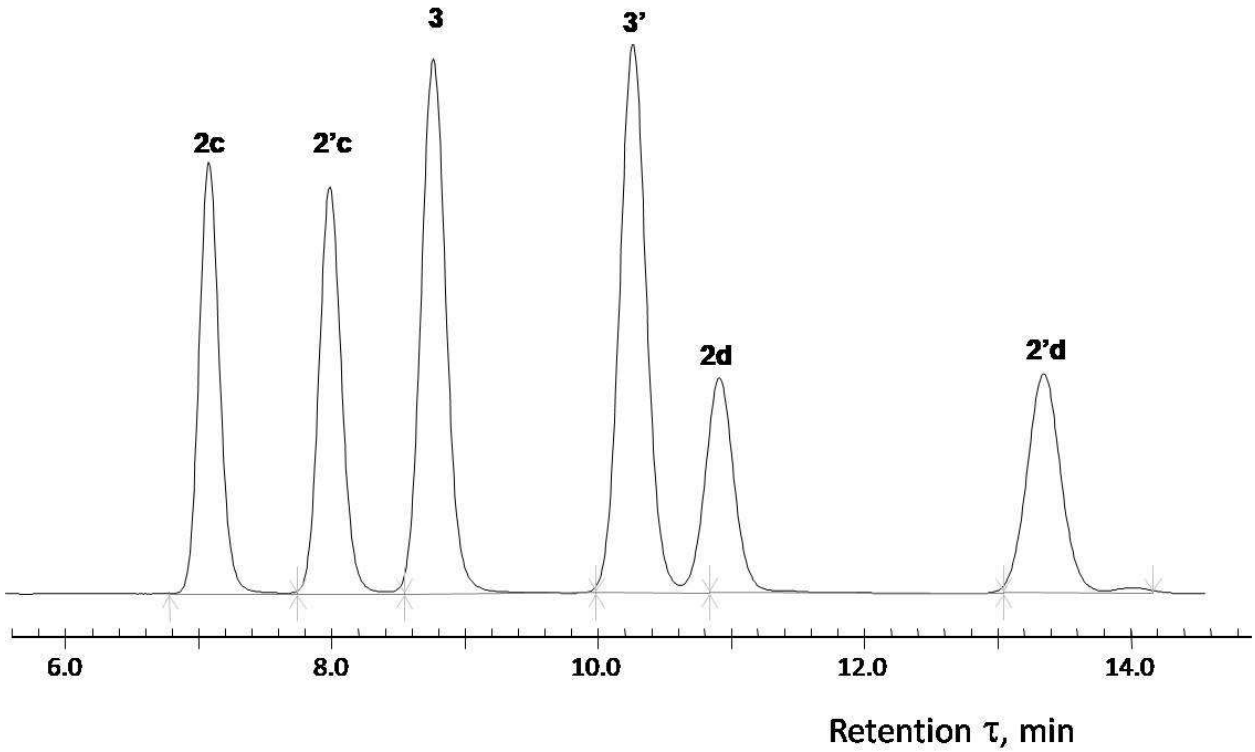
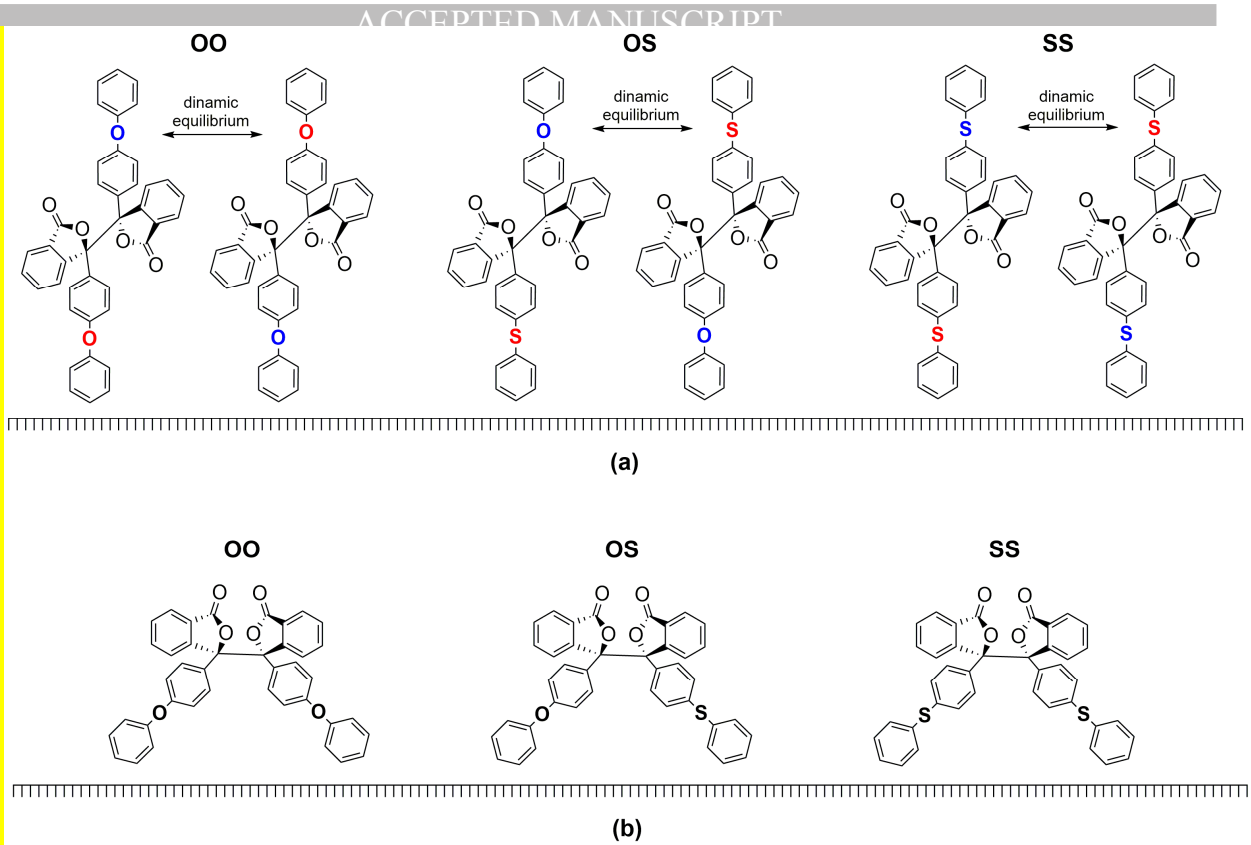



**Figure 5.** HPLC of the mixture of biaryl-3,3'-diphtalides **2c, 2'c, 2d, 2'd, 3, 3'.**

By analogy with literature data on adsorption of diastereoisomers of other classes[28-38], differences in chromatographic behavior of the diastereomeric diphthalides can be explained by a different mechanism of their adsorption, which in its turn is determined by configurational structure and preferred conformation of these compounds. It is considered, that compounds adsorbed on an adsorbent's surface posses the same conformation as in a solution[28-30]. In case of cisoid rotamers, a two-point adsorption is realized by means of two adsorption centres (polyphenylene substitutents) which are located on one side of the skeletal C3-C3' bond. In case of transoid rotamers of *meso*-diphthalides, a single-point adsorption is most probable (Figure 6).




$\tau_{OS} = \frac{\tau_{OO} + \tau_{SS}}{2}$ for both (*R*,S**)- and (*R*,R**)-diastereomeric forms. $\tau$ is a retention time

**Figure 6.** Schematic representation of a single- and two-point adsorption of *meso*- (a) and chiral (b) rotamers of biaryl-3,3'-diphthalides on a hydrophobic stationary phase.

Collating the results of X-ray analysis with 1H and 13C NMR spectra revealed the fact that determination of diastereomeric configuration of one-type biaryl-3,3'-diphthalides might be done only on the basis of spectral data. A correlation of relative configuration and conformation of the diphthalides with characteristic signals of protons and carbons of the phthalide groups allows us to do it (Table 3).

**Table 3.** Spectral characteristics of biaryl-3,3′-diphthalides **2a-g/2'a-g.**

| Entry | Prod. | Form | NMR ($CDCl_3$, ppm.) | | | IR, $cm^{-1}$ ($\nu_{C=O}$) |
|---|---|---|---|---|---|---|
| | | | H5 | C3 | C1 | |
| 1 | **2a** | (*R*,S**) | 8.43 | 90.24 | 168.85 | 1772.66 |
| | **2'a** | (*R*,R**) | 8.00 | 90.99 | 169.37 | 1768.80 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2 | **2b** | (*R*,S**) | 8.41 | 90.11 | 168.74 | 1780.37 |
| | **2'b** | (*R*,R**) | 7.98 | 90.83 | 169.27 | 1776.52 |
| 3 | **2c** | (*R*,S**) | 8.31 | 90.18 | 168.65 | 1774.59 |
| | **2'c** | (*R*,R**) | 7.95 | 90.82 | 169.10 | 1770.73 |
| 4 | **2d** | (*R*,S**) | 8.28 | 89.88 | 168.45 | 1782.30 |
| | **2'd** | (*R*,R**) | 7.93 | 90.57 | 168.92 | 1778.44 |
| 5 | **2e** | (*R*,S**) | 8.45 | 90.74 | 168.93 | 1772.66 |
| | **2'e** | (*R*,R**) | 8.02 | 91.56 | 169.57 | 1778.44 |
| 6 | **2f** | (*R*,S**) | 8.51 | 90.62 | 168.81 | 1764.94 |
| | **2'f** | (*R*,R**) | 8.08 | 91.46 | 169.42 | 1775.55 |
| 7 | **2g** | (*R*,S**) | 8.44 | 90.26 | 168.85 | 1781.34 |
| | **2'g** | (*R*,R**) | 8.02 | 90.99 | 169.38 | 1776.52 |

In 1H NMR spectra, the most characteristic and informative signals represent staying apart doublets of the protons at C5, which in case of *meso*-stereomers are always widened and registered at higher resonance frequencies (~8.4 ppm) than those of chiral isomers (~8.0 ppm). The diastereomeric effect $\Delta\delta = \delta_{meso} - \delta_{rac}$ is rather significant and definitely characterize each of the diastereoisomers. Backwards, in 13C NMR spectra, the most characteristic signals of $sp^3$-hybridized carbons C3 and carbonyl carbons C1, which resonate in fields 90 and 169 ppm correspondingly, for (*R*,S**)-diphthalides are registered at lower frequencies as compared with (*R*,R**)-isomers. The distinctions between diastereomers, apparent in 1H and 13C NMR spectra, are illustrated in Figures 7 and 8 respectively on the example of compounds **2c/2'c**. The 1H and 13C NMR spectra of all obtained biaryl-3,3′-diphthalides **2a-g/2'a-g, 3/3'** are available in supplementary materials.

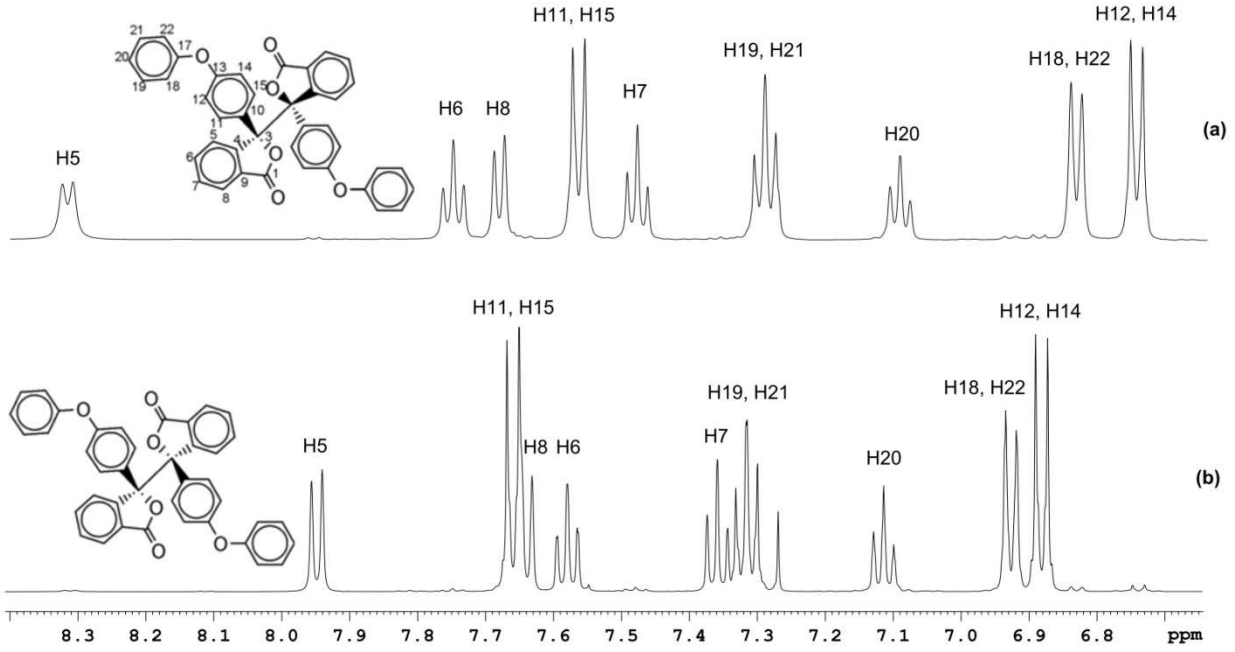



**Figure 7.** 1H NMR spectra of (*R*,S**)- (a) and (*R*,R**)- (b) 3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide.

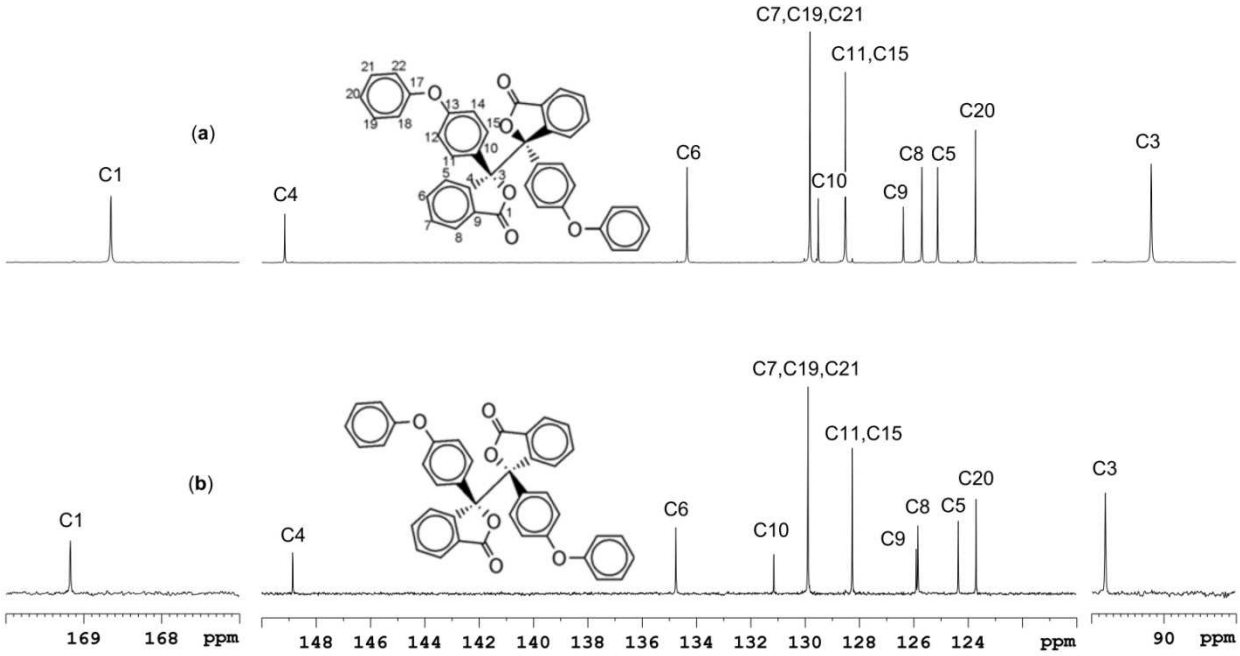



**Figure 8.** 13C NMR spectra of (*R*,S**)- (a) and (*R*,R**)- (b) 3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide.

Differences between the diastereomers appear in IR-spectra as well. Characteristic frequencies of carbonyl group's valence vibrations, for *meso*-isomers with substituents of linear polyphenylene series, are 5-7 $cm^{-1}$ less than for chiral stereoisomers (Table 3). For diastereomeric pairs with coplanar disposition of

phenylene rings in fluorene (Table 3, Entry 5) and dibenzofurane (Table 3, Entry 6) substituents, the relation is inverse. The characteristic band in the field 975 $cm^{-1}$, which had been sighted in spectrum of racemic 3,3′-diphthalides earlier[8], is also observed in case of all new diphthalides of analogous structure **2'a-g, 3'**.

## Conclusion

On the basis of the results of the conducted work we can summarize that a strong repulsion of the electronegative oxygen atoms in adjacent phthalide groups of biaryl-3,3′-diphthalides leads to retardation of C3–C3′ bond twisting and consequently causes the formation of stable conformers (rotamers) of these compounds. In case of chiral diastereomers, these are conformers with erythroid disposition of phthalide groups (***cis*** or synperiplanar rotamers), in which a dihedral angle Ar–C3–C3′–Ar′ has a value from ~40° to ~52°, and in case of *meso*-diphthalides these are threoyd conformers (***trans*** or antiperiplanar rotamers) with the dihedral angle equal to 180° (for all *meso*-diastereoisomers). Distinguishing between (*R*,S**)- and (*R*,R**)-diphthalides may be done very precisely by means of the 1H NMR spectroscopy, since the characteristic signals of the protons at C5, which are registered at ~8.4 ppm for *meso*-forms and at ~8.0 ppm for chiral forms, allow us to clearly attribute each spectrum to definite diastereoisomer.

## Experimental

*Measurements*

The IR-spectroscopy was performed on a Shimadzu IR Prestige-21 instrument. The 1H and 13C NMR spectra were recorded on a Bruker Avance III 500 MHz spectrometer, at 500 and 126 MHz correspondingly, in $CDCl_3$. The HPLC was carried on a Waters Breeze liquid chromatograph equipped with spectrophotometric detector (λ 215 nm) and Luna C18 column (10×250 mm, particle size 10 μm) at 25°C. Eluent (acetonitrile-water, 83:17) was fed with a flow rate of 4 mL $min^{-1}$. Mass spectra were obtained using Thermo Finnigan MAT 95 XP (EI, 70 eV) and Shimadzu LCMS-2010EV (CI) instruments. Elemental analyses were carried on Euro EA 3000 CHNS-analyzer.

*X-ray analysis*

The X-ray diffraction analysis of **2a**, **2'a**, **2b**, **2'b**, **2c**, **2'c**, **2d**, **2'd**, **2'e** and **2'f** was carried out on a XCalibur Eos automated four-circle diffractometer (graphite monochromator, MoKα radiation, λ = 0.71073 Å, ω-scanning, 2θmax = 62°). The data

were collected and processed using a CrysAlisPro Oxford Diffraction Ltd program[39]. The structures were solved by direct methods and refined by full-matrix least-squares method in the anisotropic approximation for non-hydrogen atoms. All hydrogen atoms are generated using the proper HFIX command and refined isotropically using the riding model. The calculations were performed using the SHELX[40] program package. The molecular plots were drawn using Mercury[41].

CCDC 1876560, 1409636, 1876841, 1876843, 1409641, 1876849, 1876571, 1876566, 1876848, 1876839 contain the supplementary crystallographic data for the structures **2a**, **2'a**, **2b**, **2'b**, **2c**, **2'c**, **2d**, **2'd**, **2'e** and **2'f** accordingly. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/datarequest/cif.

*Materials*

Commercially available starting reactants were used as received unless otherwise indicated. Acetone was stirred over dry $K_2CO_3$ overnight, then distilled and stored over 4-A molecular sieves. NaI was dried by heating. Pseudo acids chlorides **1a-g** were obtained by $AlCl_3$-promoted acylation of the corresponding aromatic compounds with phthalic anhydride followed by treatment of produced *o*-keto carboxylic acids with thionyl chloride in accordance with the procedures described in literature.[42-46]

*Biaryl-3,3'-diphthalides **2a-g/2'a-g.***

Biaryl-3,3'-diphthalides **2a-g/2'a-g** were synthesized via dimerization of pseudo monoacids chlorides **1a-g** by treatment with sodium iodide in acetone according to the published method.[8]

**(*R*,S**)-3,3'-bis(diphenyl-4-yl)-3,3'-diphthalide (2a).** Colorless crystals, mp 285.0-286.0°C (dec). IR, $cm^{-1}$: 1772.66, 1488.15, 1366.62, 1284.65, 1241.25, 1216.17, 1069.57, 1022.32, 1009.78, 993.38, 765.77, 759.02, 736.84, 717.55, 701.15. 1H NMR, δ (ppm): 7.32 (t, 2H, *J* = 7.7 Hz), 7.37 (d, 4H *J* = 8.5 Hz), 7.38 (t, 4H, *J* = 7.8 Hz), 7.43 (t, 2H, 7.6 *J* = Hz), 7.47 (d, 4H, *J* = 7.8 Hz), 7.62 (d, 2H, *J* = 7.6 Hz), 7.71 (d, 4H, *J* = 8.5 Hz), 7.77 (t, 2H, *J* = 7.7 Hz), 8.43 (d, 2H, *J* = 7.7 Hz); 13C NMR, δ (ppm): 90.24, 125.16, 125.81, 126.30, 126.47, 127.02, 127.40, 127.74, 128.86, 129.91, 134.06, 134.39, 139.85, 141.18, 149.16, 168.85.

**(*R*,R**)-3,3'-bis(diphenyl-4-yl)-3,3'-diphthalide (2'a).** Colorless crystals, mp 295.0-300.0°C (dec). IR, $cm^{-1}$: 1768.80, 1489.11, 1449.57, 1286.58, 1246.07, 1230.64, 1084.04, 993.38, 975.06, 823.64, 758.06, 735.87, 697.30. 1H NMR, δ (ppm): 7.32 (t,

2H, *J* = 7.7 Hz), 7.37 (t, 2H, *J* = 7.7 Hz), 7.40 (t, 4H, *J* = 7.8 Hz), 7.48 (d, 4H, *J* = 8.5 Hz), 7.52 (d, 4H, *J* = 8.5 Hz), 7.60 (t, 2H, *J* = 7.8 Hz), 7.65 (d, 2H, *J* = 7.7 Hz), 7.83 (d, 4H, *J* = 8.5 Hz), 8.00 (d, 2H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 90.99, 124.56, 125.81, 126.84, 126.97, 127.03, 127.06, 127.66, 128.85, 129.92, 134.79, 135.67, 140.06, 141.16, 149.11, 169.37. Found, %: C 84.05; H 4.35. $M^+$ 570.1826 (EI). Anal. Calcd for $C_{40}H_{26}O_4$, %: C 84.19; H 4.59. *M* 570.1826.

**(*R*,S**)-3,3'-bis[4-(*p*-bromophenyl)phenyl]-3,3'-diphthalide (2b).** Colorless crystals, mp 315.0-320.0℃ (dec). IR, $cm^{-1}$: 1780.37, 1593.17, 1481.95, 1287.80, 1248.00, 1074.40, 1001.10, 807.24, 747.45. 1H NMR, δ (ppm): 7.32 (d, 4H, *J* = 8.2 Hz), 7.33 (d, 4H, *J* = 8.1 Hz), 7.45 (t, 2H, *J* = 7.5 Hz), 7.51 (d, 4H, *J* = 8.4 Hz), 7.63 (d, 2H, *J* = 7.6 Hz), 7.71 (d, 4H, *J* = 8.5 Hz), 7.78 (t, 2H, *J* = 7.6 Hz), 8.41 (d, 2H, *J* = 7.6 Hz); 13C NMR, δ (ppm): 90.11, 122.09, 125.10, 125.86, 126.22, 126.30, 127.52, 128.60, 130.01, 131.98, 134.48, 138.72, 140.03, 149.05, 168.74.

**(*R*,R**)-3,3'-bis[4-(*p*-bromophenyl)phenyl]-3,3'-diphthalide (2'b).** Colorless crystals, mp 280.0-285.0℃ (dec). IR, $cm^{-1}$: 1776.52, 1592.00, 1483.32, 1286.58, 1246.07, 1226.78, 1102.37, 1080.18, 1002.06, 995.31, 976.02, 811.10, 733.95, 685.72. 1H NMR, δ (ppm): 7.36 (t, 2H, *J* = 7.2 Hz), 7.37 (d, 4H, *J* = 8.5 Hz), 7.44 (d, 4H, *J* = 8.6 Hz), 7.52 (d, 4H, *J* = 8.5 Hz), 7.60 (t, 2H, *J* = 7.7 Hz), 7.65 (d, 2H, *J* = 8.6 Hz), 7.84 (d, 4H, *J* = 8.6 Hz), 7.98 (d, 2H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 90.83, 122.01, 124.49, 125.66, 128.86, 126.69, 127.02, 128.61, 130.01, 131.97, 134.86, 136.17, 138.89, 139.94, 148.97, 169.27. Found, %: C 65.70; H 3.25; Br 21.93. $[M/2]^+$ 363.0021 (EI); $[M+H]^+$ 727 (CI). Anal. Calcd for $C_{40}H_{24}O_4Br_2$, %: C 65.95; H 3.32; Br 21.94. *M* 726.0036.

**(*R*,S**)-3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide (2c)**. Colorless crystals, mp 220.5-221.0℃. IR, $cm^{-1}$: 1774.59, 1587.48, 1505.51, 1489.11, 1456.32, 1288.50, 1241.25, 1202.67, 1167.95, 1098.51, 1073.47, 1022.32, 1003.03, 994.35, 869.93, 742.63. 1H NMR, δ (ppm): 6.75 (d, 4H, *J* = 8.8 Hz), 6.83 (d, 4H, *J* = 8.1 Hz), 7.09 (t, 2H, *J* = 7.4 Hz), 7.29 (t, 4H, *J* = 7.8 Hz), 7.48 (t, 2H, *J* = 7.5 Hz), 7.56 (d, 4H, *J* = 8.8 Hz), 7.68(d, 2H, *J* = 7.6 Hz), 7.75 (t, 2H, *J* = 7.6 Hz), 8.31 (d, 2H, *J* = 7.6 Hz); 13C NMR, δ (ppm): 90.18, 117.86, 119.12, 123.73, 125.12, 125.70, 126.39, 128.52, 129.52, 129.82, 134.35, 149.15, 156.50, 157.50, 168.65.

**(*R*,R**)-3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide (2'c)**. Colorless crystals, mp 211.0-212.0℃. IR, $cm^{-1}$: 1770.73, 1587.48, 1505.51, 1487.18, 1366.62, 1332.87, 1307.79, 1287.54, 1248.96, 1202.67, 1169.88, 1102.37, 1079.22, 1067.65, 1021.35, 1003.03, 996.28, 973.13, 738.77. 1H NMR, δ (ppm): 6.88 (d, 4H, *J* = 8.9 Hz), 6.92 (d, 4H, *J* = 7.8 Hz), 7.11 (t, 2H, *J* = 7.4 Hz), 7.31 (t, 4H, *J* = 7.7 Hz), 7.36 (t, 2H, *J* = 7.5 Hz),

7.58 (t, 2H, *J* = 7.8 Hz), 7.63 (d, 2H, *J* = 7.7 Hz), 7.65 (d, 4H, *J* = 8.9 Hz), 7.95 (d, 2H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 90.82, 118.19, 119.09, 123.65, 124.37, 125.86, 125.93, 128.27, 129.77, 129.78, 129.89, 134.70, 149.40, 156.70, 157.53, 169.10. Found, %: C 79.63; H 4.26. $M^+$ 602.1684 (EI). Anal. Calcd for $C_{40}H_{26}O_6$, %: C 79.72; H 4.35. *M* 602.1724.

**(*R*,S**)-3,3'-bis[4-(phenylthio)phenyl]-3,3'-diphthalide (2d)**. Colorless crystals, mp 227.0-227.5℃. IR, $cm^{-1}$: 1782.30, 1580.81, 1477.54, 1244.14, 1069.57, 1020.39, 1008.81, 745.52, 701.15. 1H NMR, δ (ppm): 7.02 (d, 4H, *J* = 8.6 Hz), 7.19 (d, 4H, *J* = 7.5 Hz), 7.25-7.30 (m, 6H), 7.47 (t, 2H, *J* = 7.6 Hz), 7.50 (d, 4H, *J* = 8.6 Hz), 7.66 (d, 2H, *J* = 7.6 Hz), 7.73 (t, 2H, *J* = 7.5 Hz), 8.28 (d, 2H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 89.88, 125.02, 125.34, 125.73, 126.22, 127.56, 127.64, 129.32, 129.94, 131.78, 133.27, 134.27, 134.42, 137.51, 148.73, 168.45.

**(*R*,R**)-3,3'-bis[4-(phenylthio)phenyl]-3,3'-diphthalide (2'd)**. Colorless crystals, mp 166.0-166.5℃. IR, $cm^{-1}$: 1778.44, 1594.3, 1492.27, 1477.54, 1286.58, 1247.03, 1244.85, 1039.69, 1084.04, 1020.39, 1003.99, 993.38, 927.16, 812.07, 753.23, 722.37, 691.51. 1H NMR, δ (ppm): 7.16 (d, 4H, *J* = 8.6 Hz), 7.25-7.30 (m, 10H), 7.34 (t, 2H, *J* = 7.5 Hz), 7.56 (t, 2H, *J* = 7.5 Hz), 7.62 (d, 2H, *J* = 7.6 Hz), 7.63 (d, 4H, *J* = 8.6 Hz), 7.93 (d, 2H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 90.57, 124.36, 125.76, 125.80, 127.22, 127.62, 129.38, 129.73, 129.96, 131.75, 134.48, 134.76, 135.02, 137.28, 148.49, 168.92. Found, %: C 75.80; H 3.91; S 10.00. $M^+$ 634.1267 (EI). Anal. Calcd for $C_{40}H_{26}O_4S_2$, %: C 75.69; H 4.13; S 10.10. *M* 634.1263.

**(*R*,S**)-3,3'-bis(fluoren-2-yl)-3,3'-diphthalide (2e)**. Yellowish powder, mp 276.0-280.0℃ (dec). IR, $cm^{-1}$: 1772.66, 1595.07, 1455.35, 1403.27, 1284.65, 1235.46, 1103.33, 1072.47, 1018.46, 993.38, 752.27, 741.66, 732.02. 1H NMR, δ (ppm): 3.68 (d, 2H, *J* = 21.8 Hz), 3.82 (d, 2H, *J* = 21.8 Hz), 7.30 (t, 2H, *J* = 7.4 Hz), 7.34 (t, 2H, *J* = 7.2 Hz), 7.39 (t, 2H, *J* = 7.5 Hz), 7.50 (d, 2H, *J* = 7.3 Hz), 7.54 (d, 2H, *J* = 8.4 Hz), 7.55 (d, 2H, *J* = 8.4 Hz), 7.68 (d, 4H, *J* = 7.8 Hz), 7.76 (t, 2H, *J* = 7.9 Hz), 7.82 (s, 2H), 8.45 (d, 2H, *J* = 7.5 Hz); 13C NMR, δ (ppm): 36.92, 90.74, 119.20, 120.27, 123.75, 125.14, 125.29, 125.73, 128.79, 126.37, 126.90, 127.25, 129.76, 133.48, 134.17, 140.81, 141.91, 142.79, 143.65, 149.40, 168.93.

**(*R*,R**)-3,3'-bis(fluoren-2-yl)-3,3'-diphthalide (2'e)**. Yellowish crystals, mp 288.0-290.0℃ (dec). IR, $cm^{-1}$: 1778.44, 1591.96, 1465.32, 1284.65, 1248.96, 1223.89, 1103.33, 1096.58, 1006.89, 983.74, 761.91, 736.84, 685.43. 1H NMR, δ (ppm): 3.74 (d, 2H, *J* = 21.8 Hz), 3.81 (d, 2H, *J* = 21.8 Hz), 7.27 (t, 2H, *J* = 8.2 Hz), 7.32 (t, 2H, *J* = 7.3 Hz), 7.36 (t, 2H, *J* = 7.3 Hz), 7.48 (d, 2H, *J* = 7.4 Hz), 7.59(d, 2H, *J* = 7.9 Hz), 7.60 (t,

2H, *J* = 7.2 Hz), 7.66 (d, 2H, *J* = 7.6 Hz), 7.68 (d, 2H, *J* = 7.5 Hz), 7.77 (d, 2H, *J* = 8.3 Hz), 7.92 (s, 2H), 8.02 (d, 2H, *J* = 7.9 Hz); 13C NMR, δ (ppm): 37.03, 91.56, 119.53, 120.18, 123.11, 124.72, 125.07, 125.29, 125.75, 125.77, 126.81, 127.10, 129.82, 134.71, 135.12, 140.88, 141.92, 143.12, 143.59, 149.44, 169.57. Found, %: C 84.00; H 4.07. $M^+$ 594.1832 (EI). Anal. Calcd for $C_{42}H_{26}O_4$, %: C 84.83; H 4.41. *M* 594.1826.

**(*R*,S**)-3,3'-bis(dibenzofuran-2-yl)-3,3'-diphthalide (2f)**. White powder, mp 336.0-338.0℃ (dec). IR, $cm^{-1}$: 1764.94, 1595.12, 1450.03, 1273.17, 1242.21, 1201.70, 1077.29, 999.17, 744.55, 723.34. 1H NMR, δ (ppm): 7.35 (t, 2H, *J* = 6.8 Hz), 7.37 (d, 2H, *J* = 8.5 Hz), 7.39 (t, 2H, *J* = 6.8 Hz), 7.45 (t, 2H, *J* = 8.2 Hz), 7.51 (d, 2H, *J* = 8.2 Hz), 7.55 (d, 2H, *J* = 7.5 Hz), 7.78 (t, 2H, *J* = 8.2 Hz), 7.84 (d, 2H, *J* = 8.8 Hz), 7.90 (d, 2H, *J* = 7.4 Hz), 8.21 (s, 2H), 8.51 (d, 2H, *J* = 7.6 Hz); 13C NMR, δ (ppm): 90.62, 111.11, 111.81, 119.65, 120.81, 123.08, 123.82, 123.95, 125.15, 125.89, 125.98, 126.24, 127.66, 129.89, 129.98, 134.40, 149.43, 155.81, 156.60, 168.81.

**(*R*,R**)-3,3'-bis(dibenzofuran-2-yl)-3,3'-diphthalide (2'f).** Colorless crystals, mp 285.0-290.0℃ (dec). IR, $cm^{-1}$: 1775.55, 1592.20, 1447.64, 1279.82, 1247.03, 1203.63, 1104.29, 1008.81, 999.17, 980.84, 753.23, 747.45, 728.16. 1H NMR, δ (ppm): 7.29 (t, 2H, *J* = 8.2 Hz), 7.38 (t, 2H, *J* = 7.3 Hz), 7.39 (t, 2H, *J* = 7.4 Hz), 7.40 (d, 2H, *J* = 8.8 Hz), 7.45 (d, 2H, *J* = 8.2 Hz), 7.63 (t, 2H, *J* = 7.6 Hz), 7.68 (d, 2H, *J* = 7.6 Hz), 7.89 (d, 2H, *J* = 7.7 Hz), 7.99 (d, 2H, *J* = 8.8 Hz), 8.08 (d, 2H, *J* = 7.8 Hz), 8.30 (s, 2H); 13C NMR, δ (ppm): 91.46, 111.47, 111.69, 118.83, 120.87, 122.92, 123.83, 124.18, 124.70, 125.58, 125.65, 125.86, 127.51, 129.93, 131.48, 134.82, 149.49, 155.79, 156.52, 169.42. Found, %: C 80.95; H 3.34. $M^+$ 598.1417 (EI). Anal. Calcd for $C_{40}H_{22}O_6$, %: C 80.26; H 3.70. *M* 598.1411.

**(*R*,S**)-3,3'-bis(terphenyl-4-yl)-3,3'-diphthalide (2g)**. White powder, mp 290.0-294.0℃ (dec). IR, $cm^{-1}$: 1781.34, 1594.32, 1485.58, 1247.12, 1074.40, 1003.03, 816.89, 765.77, 745.52, 700.19. 1H NMR, δ (ppm): 7.37 (t, 2H, *J* = 7.2 Hz), 7.43-7.47 (m, 10H), 7.56 (d, 4H, *J* = 8.2 Hz), 7.61-7.65 (m, 10H), 7.74 (d, 4H, *J* = 8.4 Hz), 7.79 (t, 2H, *J* = 7.6 Hz), 8.44 (d, 2H, *J* = 7.1 Hz); 13C NMR, δ (ppm): 90.26, 125.17, 126.34, 127.10, 127.36, 127.47, 127.53, 127.59, 128.91, 129.00, 129.94, 134.13, 134.42, 138.67, 140.58, 140.63, 149.15, 168.85.

**(*R*,R**)-3,3'-bis(terphenyl-4-yl)-3,3'-diphthalide (2'g)**. White powder, mp 309.0-312.0℃ (dec). IR, $cm^{-1}$: 1776.52, 1595.20, 1484.29, 1366.62, 1285.61, 1247.03, 1098.51, 1077.29, 1003.03, 993.38, 972.16, 815.92, 763.84, 745.52, 697.30. 1H NMR, δ (ppm): 7.35-7.40 (m, 4H), 7.46 (t, 4H, *J* = 7.6 Hz), 7.55 (d, 4H, *J* = 8.5 Hz), 7.60-7.68 (m, 16H), 7.87 (d, 4H, *J* = 8.5 Hz), 8.02 (d, 4H, *J* = 7.8 Hz); 13C NMR, δ (ppm): 90.99,

124.56, 125.79, 125.83, 126.71, 127.04, 127.09, 127.40, 127.49, 127.58, 128.89, 129.95, 134.82, 135.73, 138.89, 140.52, 140.61, 149.08, 169.38. Found, %: C 86.65; H 4.45. $[M+H]^+$ 723 (CI). Anal. Calcd for $C_{52}H_{34}O_4$, %: C 86.41; H 4.74. *M* 722.2452.

*3-(4-phenoxyphenyl)-3'-[4-(phenylthio)phenyl]-3,3'-diphthalides* ***(3/3').***

A solution of 25.0 g sodium iodide (0.17 mol) in dry acetone (100 mL) was added to a stirred solution of mixture of 15.0 g *o*-[*p*-(phenylthio)-benzoyl]-benzoic pseudo acid chloride (42.5 mmol) and 14.3 g *o*-(*p*-phenoxybenzoyl)-benzoic pseudo acid chloride (42.5 mmol) in acetone (200 mL). Stirring was continued for 4h, then reaction mixture was poured into solution of $Na_2S_2O_3 \cdot 5H_2O$ (90 g) in water (450 ml) to remove the liberated iodine. Insoluble solid was filtered off and washed with water. The solid was stirred in 10 % KOH solution (500 mL) for 1 h, then washed with water until neutral, and then dried. General yield 23.7 g (90%). Isolation of individual diphthalides **3** and **3'** was performed using semi-preparative HPLC.

**(*R*,S**)-3-(4-phenoxyphenyl)-3'-[4-(phenylthio)phenyl]-3,3'-diphthalide (3)**. Colorless crystals, mp 215-216℃. IR, $cm^{-1}$: 1782.30, 1580.10, 1490.07, 1466.93, 1377.23, 1286.58, 1231.60, 1168.91, 1067.65, 1007.85, 860.60, 759.02, 745.52, 710.80. 1H NMR, δ (ppm): 6.73 (d, 2H, *J* = 8.8 Hz), 6.83 (d, 2H, *J* = 8.2 Hz), 7.03 (d, 2H, *J* = 8.5 Hz), 7.09 (t, 1H, *J* = 7.4 Hz), 7.19 (d, 2H, *J* = 7.4 Hz), 7.30-7.26 (m, 6H), 7.47 (t, 2H, *J* = 7.5 Hz), 7.53 (t, 4H, *J* = 8.8 Hz), 7.67 (d, 2H, *J* = 7.6 Hz), 7.74 (t, 2H, *J* = 7.6 Hz), 8.30 (d, 2H, *J* = 7.6 Hz); 13C NMR, δ (ppm): 90.03, 90.06, 123.76, 125.09, 125.72, 125.77, 126.29, 126.32, 127.57, 127.63, 128.56, 129.35, 129.42, 129.84, 129.89, 129.93, 131.78, 133.45, 134.37, 134.40, 134.42, 137.43, 148.89, 149.02, 156.44, 157.52, 168.57, 168.63.

**(*R*,R**)-3-(4-phenoxyphenyl)-3'-[4-(phenylthio)phenyl]-3,3'-diphthalides (3')**. Colorless crystals, mp 180-181℃. 1H NMR, δ (ppm): 6.87 (d, 2H, *J* = 8.8 Hz), 6.92 (d, 2H, *J* = 8.5 Hz), 7.12 (t, 1H, *J* = 7.4 Hz), 7.17 (d, 2H, *J* = 8.5 Hz), 7.26-7.29 (m, 5H), 7.31 (t, 2H, *J* = 7.4 Hz), 7.35 (t, 2H, *J* = 7.4 Hz), 7.57 (t, 2H, *J* = 7.7 Hz), 7.65-7.59 (m, 6h), 7.93 (d, 1H, *J* = 7.7 Hz), 7.94 (d, 1H, *J* = 7.7 Hz); 13C NMR, δ (ppm): 90.70, 90.74, 123.74, 124.37, 124.39, 125.85, 127.33, 127.61, 128.18, 129.35, 129.40, 129.85, 129.90, 129.93, 129.98, 131.05, 131.70, 134.62, 134.78, 134.80, 135.18, 137.18, 148.59, 148.78, 156.62, 157.53, 169.06, 169.11. Found, %: C 77.46; H 4.01; S 5.00. $[M+H]^+$ 619 (CI). Anal. Calcd for $C_{40}H_{26}O_5S$, %: C 77.65; H 4.24; S 5.18. *M* 618.1495.

## Acknowledgements

Authors are grateful to Dr Yu.A.Lebedev of IMCP UFRC RAS for kindly making the microscopic image of the crystal of (*R*,R**)-3,3'-bis[4-(phenylthio)phenyl]-3,3'-diphthalide in polarized light.

The IR-, NMR-analyses and HPLC were performed on equipment at the Centre for the Collective Use “Chemistry” of UIC UFRC RAS. The X-ray analyses were carried out on equipment at the Centre for the Collective Use “Agidel” of IPC UFRC RAS.

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**Table 1.** Synthesis of biaryl-3,3'-diphtalides **2a-g/2'a-g.**

**Table 2.** Structural characteristics of biaryl-3,3'-diphtalides **2a-d/2'a-f** from the X-ray analyses data.

**Table 3.** Spectral characteristics of biaryl-3,3′-diphthalides **2a-g/2'a-g.**

**Figure 1.** Molecular structures of biaryl-3,3′-diphthalides. Atoms are represented by thermal displacement ellipsoids at the 30% probability level.

**Figure 2.** Favorable rotameric conformation of biaryl-3,3′-diphthalides diastereoisomers.

**Figure 3.** Plastic deformation of a platy crystal of (*R*,R**)-3,3'-bis[4-(phenylthio)phenyl]-3,3'-diphthalide observed in polarized light.

**Figure 4.** Molecular packing along the crystallographic axes for (*R*,S**)- and (*R*,R**)-biaryl-3,3'-diphthalide crystals **2a/2'a, 2b/2'b, 2c/2'c** and **2d/2'd.**

**Figure 5.** HPLC of the mixture of biaryl-3,3'-diphtalides **2c, 2'c, 2d, 2'd, 3, 3'.**

**Figure 6.** Schematic representation of a single- and two-point adsorption of *meso*- (a) and chiral (b) rotamers of biaryl-3,3'-diphthalides on a hydrophobic stationary phase.

**Figure 7.** 1H NMR spectra of (*R*,S**)- (a) and (*R*,R**)- (b) 3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide.

**Figure 8.** 13C NMR spectra of (*R*,S**)- (a) and (*R*,R**)- (b) 3,3'-bis(4-phenoxyphenyl)-3,3'-diphthalide.

**Scheme 1.** Preparation of *o*-aroylbenzoic pseudo acids chlorides **1a-g**.

**Scheme 2.** Joint dimerization of pseudo acids chlorides **1c** and **1d**.