

Zakład Stereo- i Spektrochemi  
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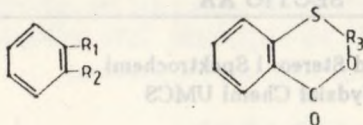
**Effect of Molecular Structure on Optical Properties of Sulphoxide Systems. 2-/4' -Methylbenzylsulphinyl/benzoic Acids and Some of Their Derivatives. Part I**

Wpływ budowy cząsteczkowej na właściwości optyczne układów sulfotlenkowych. Kwasy 2-/4' - metylobenzylsulfinylo/benzoesowe i ich niektóre pochodne. Część I

The problem of the effect of position isomerism of certain substituents and functional groups in aromatic rings on optical properties of aromatic-aliphatic systems containing heteroatomic chirality centers separated from aromatic fragments of molecules by methylene groups has been studied in our laboratory on the examples of benzylsulfinylacetic and ortho-benzylsulfinylbenzoic acids and their derivatives. The observed optical order in the group of isomeric bromobenzylsulfinylacetic acids [1-4] as well as in the group of isomeric ortho-bromobenzylsulfinylbenzoic acids [5-8] suggested that a single methylene group does not isolate completely the chiral sulfoxide systems from the effects caused by substituents in aromatic ring. The observed optical and stereochemical relationships encouraged us to further studies in the group of compounds with methyl groups as substituents in arene nuclei. A closer determination of optical relationships in this group of still little known systems can be of special interest.

Our investigations were started with a comparative study of principal chiroptical properties of 2-(benzylsulfinyl)benzoic acids and their methyl derivatives with methyl group in the benzene ring of benzyl moiety i.e. isomeric 2-(methylbenzylsulfinyl)benzoic acids. In the present communication we are reporting the synthesis and the determination of principal stereochemical properties of enantiomeric 2-(4'-methylbenzylsulfinyl)benzoic acids and their simple derivatives.

The starting material was 2-(4'-methylbenzylthio)benzoic acid (1) which was obtained in a good yield by coupling 2-mercaptobenzoic acid [18] with p-methylbenzyl bromide in alkaline medium. The structure of acid 1 was confirmed by its IR spectrum (the characteristic bands are quoted in the Experimental Part).



- |  |  |
|--|--|
| 1. $R_1 = \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$   | $R_2 = \text{COOH}$  |
| 2. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{COOH}$  |
| 3. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{CO} \cdot \text{OCH}_3$   |
| 4. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{CO} \cdot \text{NH} \cdot \text{CH}_3$  |
| 5. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{CO} \cdot \text{OCH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{Br} / p/$ |
| 6. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{CO} \cdot \text{OCH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 / p/$               |
| 7. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{COOH} \cdot \text{Bruc.}$   |
| 8. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{COOH}$  |
| 9. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$  | $R_2 = \text{COOH} \cdot \text{Strych.}$   |
| 10. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{COOH}$  |
| 11. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{CO} \cdot \text{OCH}_3$   |
| 12. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{CO} \cdot \text{NH} \cdot \text{CH}_3$  |
| 13. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{CO} \cdot \text{OCH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{Br} / p/$ |
| 14. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{CO} \cdot \text{OCH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 / p/$               |
| 15. $R_1 = \text{SO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$ | $R_2 = \text{COOH}$  |
| 16. $R_1 = \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$   |  |
| 17. $R_1 = \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3$                   |  |

Racemic 2-(4'-methylbenzylsulfinyl)benzoic acid (2) was obtained by oxidation of the compound 1 with 30% hydrogen peroxide in glacial acetic acid at room temperature. When acid 1 was treated with an excess of the oxidizing agent at elevated temperature a good yield of sulfone 15 was obtained. (The IR spectra confirming the structures of the two oxidation products are shown in the Experimental Part). Racemic acid 2 was characterized as its methylamide (4) and methyl (3), p-bromophenacyl (5) and p-nitrobenzyl (6) esters.

Racemic 2-(4'-methylbenzylsulfinyl)benzoic acid (2) was resolved by crystallization of diastomeric salts with optically active bases. For this purpose the neutral salts of brucine and strychnine were the most suitable. During fractional crystallization of the brucine salt from acetone the first fractions contained the salt of the laevorotatory acid whereas the dextrorotatory enantiomer could be separated from the racemate by crystallization of the salt with strychnine from 96% ethanol.

Optically active 2-(4'-methylbenzylsulfinyl)benzoic acids (8 and 10) separated from alkaloid salts and purified from benzene showed the following specific rotations 8:  $(\alpha)_D^{20} = -480, 0^\circ$  and 10:  $(\alpha)_D^{20} = +480, 0^\circ$  (96% ethanol).

Tab. 1. Thermodynamic characterization of racemization of the optically active 2-(4'-methylbenzylsulfinyl)benzoic acids

Racemization temperature °C	Racemization constants $K \times 10^5 \text{ sek}^{-1}$	Activation entropy $\Delta S^\ddagger (\text{eu})$	Activation enthalpy $\Delta H^\ddagger (\text{kcal/mole})$
15	22,79±0,02	4,75±0,01	23,03±0,01
17	29,56±0,03	4,74±0,01	23,01±0,01
19	39,37±0,04	4,73±0,01	23,01±0,01
21	50,52±0,05	4,72±0,01	23,01±0,01
23	71,26±0,06	4,71±0,01	23,02±0,01

Mixing of **8** and **10** in equimolar proportions followed by crystallisation caused the regeneration of racemic acid **2**. The melting point of the racemate **2** is a little lower ( $\Delta t = -1^\circ\text{C}$ ) than that of the antipodes **8** and **10**. The IR spectrum of racemic acid **2** was not different in the fingerprint region from the spectra of enantiomers **8** and **10**. The relatively easy resolution of optically inactive acid **2** into enantiomers (**8** and **10**) and the physical properties quoted above indicate that racemic acid **2** belongs to the type of racemic solid solution.

Optically active 2-(4'-methylbenzylsulfinyl)benzoic acids **8** and **10** possess a considerable resistance to racemization in alkaline media, but lose quite rapidly the ability to rotate the plane of polarized light in organic solvents in the presence of concentrated hydrochloric acid. Racemization processes of 2-(4'-methylbenzylsulfinyl)benzoic acids were studied using a mixture (2:1 V/V) of dioxane and dilute (3:2 V/V HCl:H<sub>2</sub>O) hydrochloric acid. In these conditions racemization of optically active acids **8** and **10** occurred according to the kinetic equation for the first order reactions ( $K = [1]/[t] \ln[\alpha_0]/[\alpha]$ ). The racemization constants (K), the activation entropies ( $\Delta S^\ddagger$ ) and the activation enthalpies ( $\Delta H^\ddagger$ ) calculated by the method of least squares, are shown in Table 1. The activation parameters of the racemization processes have been determined by the classical kinetic methods on the basis of the Eyring equation [9].

The activation energy ( $E_a$ ) and the preexponential factor ( $A = K_{max}$ ) have been determined from the empirical Arrhenius equation:  $K = A x e^{-E_a/RT}$  ( $E_a = 23.60$  kcal/mole,  $A = 1804,4 \times 10^{11} \text{ sec}^{-1}$ ). The positive values of the activation entropy ( $\Delta S^\ddagger > 0$ ) indicate that in the transition state of the racemization process additive compounds or intermediate compounds previously proposed for arylalkylsulfoxides by German [10,11,12] and American [13,14] authors are not formed.

Racemic 2-(4'-methylbenzylsulfinyl)benzoic acid **2** according to expectations has been transformed by heating with acetic anhydride into optically inactive 3-(4'-methylphenyl)-4-thiaisochroman-1-one (**16**). The structure of 3-(4'-methylphenyl)-4-thiaisochroman-1-one (**16**) was confirmed by elemental analysis and spectral method (IR spectra are shown in the Experimental Part). We have also transformed (by using acetic anhydride under the some conditions) laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid. In this way we have obtained laevorotatory 3-(4'-methylphenyl)-4-thiaisochroman-1-one (**17**),  $(\alpha)_D^{20} = -10,0^\circ$  (in 96%

ethanol) with 40% yield. It is to underline that the product of Pummerer's rearrangement in the case of unsubstituted acid [5] 2-(4'-(benzylsulfinyl)benzoic acid) rotates the plane of polarized light in the visible part of the spectrum in the reverse direction than the starting compound, what is not observed in the case of 2-(4'-methylbenzylsulfinyl)benzoic acid. Accumulating a larger number of experimental facts will give us the chance to draw more general conclusions.

In order to obtain larger comparative material for chiroptical studies we have prepared the following derivatives of laevorotatory acid **8**: methylamide (**12**) and methyl ester (**11**), p-bromophenacyl ester (**13**) and p-nitrobenzyl ester (**14**). The mild conditions under which the reactions were carried out were not likely to cause racemization at the asymmetric sulfur atom. The molar rotations of laevorotatory acid **8** and its derivatives (**11**, **12**, **13** and **14**) were determined in the spectral region  $360, 0 < \lambda < 623, 4$  nm using methanol (M), 96% ethanol (E), acetone (A), chloroform (Ch) and dioxane (D) as solvents. The results are shown in Table 2.

As it appears from the comparison of the numerical values given in this Table, the nature of solvent has not any considerable effect on the value of molar rotation. Within the visible part of the spectrum the effects of the solvents can be arranged in the following order, according to the decreasing numerical value of molar rotation:

a) for free acid:  $D(C_4H_8O_2) > A((CH_3)_2CO) > Ch(CHCl_3) > E(C_2H_5OH) > M(CH_3OH)$ ;

b) for methylamide:  $A > M > E > D > Ch$ ;

c) for methyl ester:  $A > D > Ch > M > E$ ;

d) for p-bromophenacyl and p-nitrobenzyl esters:  $D > A > Ch > M > E$ .

An analysis of the numerical data summarized in Table 2 indicates that the curves representing functions  $1/\alpha(\lambda^2)$  in the region  $0 \leq \lambda \leq 623, 4$  nm for laevorotatory acid **8** and its derivatives **11**, **12**, **13** and **14** are almost straight lines. This leads to the conclusion that the optical rotatory dispersion of the compounds examined (within the visible part of the spectrum) has the character of normal dispersion.

The comparison of Freudenberg optical shifts presented in Table 3 and molar rotation changes caused by changes in the character solvent which are summarized in Table 4 and 5, indicates that the spatial configuration of dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (**10**) is R(+).

As configuration standards were taken into account dextrorotatory 2-(benzylsulfinyl)benzoic acid [5] and 2-(3'- and 4'-bromobenzylsulfinyl)benzoic acids [6,7,15] as well as their ester derivatives having spatial configurations R(+).

On the basis of the numerical data ( $400 \leq \lambda \leq 623, 4$  nm) summarized in Table 2 functions (in four solvents) (M) ( $\lambda$ ) have been calculated for dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid. These functions have the character of the following five-term equations<sup>1</sup>:

<sup>1</sup>The equations were determined by the method of least squares using the algorithm of conjugated gradients for finding the function of many variables (computer ODRA-1204).

Tab. 2. Optical rotatory dispersion of laevorotatory 2-(4'-methylbenzylsulphinyl)benzoic acid and some of its derivatives

Compound	Solvent*	Molar rotation (M) <sup>20</sup> λ [nm]							
		623.4	589.4	579.1	546.1	520.0	480.0	440.0	435.8
Laevorotatory 2-(4'-methylbenzylsulphinyl) benzoic	A	1163.1 (1161.7)	1366.1 (1362.5)	1426.5 (1432.6)	1700.9 (1701.8)	1975.1 (1975.9)	2567.6 (2566.3)	3549.7 (3546.3)	3686.9 (3687.8)
	Ch	1138.4 (1137.3)	1327.7 (1328.5)	1398.0 (1396.1)	1651.4 (1658.5)	1922.9 (1929.5)	2523.7 (2518.6)	3489.3 (3494.1)	3642.9 (3634.5)
	D	1168.6 (1169.2)	1374.3 (1371.2)	1434.7 (1442.1)	1711.7 (1714.1)	1991.6 (1992.1)	2595.1 (2594.6)	3604.6 (3604.9)	3752.7 (3752.0)
	E	1130.2	1315.2	1388.1	1645.9	1903.8	2452.4	3346.7	3456.4
	M	1124.7	1311.3	1382.6	1635.0	1903.8	2425.0	3308.3	3434.5
			1120.9	1311.3	1377.5	1630.4	1885.7	2428.6	3310.5
Methyl ester of laevorotatory 2-(4'-methylbenzylsulphinyl) benzoic acid	A	1280.3	1473.5	1545.6	1816.6	2087.6	2698.9	3662.0	3800.4
	Ch	1121.7	1314.9	1372.5	1632.1	1900.3	2474.0	3425.6	3552.5
	D	1185.1	1378.3	1441.7	1701.3	1983.8	2589.4	3587.1	3725.5
	E	1064.0	1254.3	1326.4	1568.6	1816.6	2322.7	3212.2	3333.3
	M	1104.4	1297.6	1352.4	1614.8	1857.0	2393.3	3275.6	3416.8
			1272.7	1522.6	1593.3	1894.9	2206.1	2884.8	3959.6
p-Bromophenacyl ester of laevorotatory 2-(4'-methylbenzylsulphinyl) benzoic acid	A	1258.6	1508.4	1569.7	1876.1	2196.6	2875.4	3940.7	4176.4
	Ch	1319.9	1536.7	1607.4	1932.7	2243.8	2955.5	4138.7	4317.8
	D	1183.2	1376.4	1447.1	1711.1	1993.9	2616.2	3610.8	3771.0
	E	1187.9	1395.3	1456.6	1720.5	2003.4	2630.3	3615.5	3785.2
	M	1265.2	1457.6	1523.1	1801.5	2096.3	2751.4	3824.2	3988.0
			1162.8	1375.7	1457.6	1740.1	2030.8	2661.4	3730.0
p-Nitrobenzyl ester of laevorotatory 2-(4'-methylbenzylsulphinyl) benzoic acid	A	1277.5	1474.0	1531.3	1830.2	2149.6	2800.6	3934.7	4094.4
	Ch	1097.3	1277.5	1342.9	1596.8	1858.9	2423.9	3365.6	3488.4
	D	1138.2	1334.8	1408.9	1670.5	1940.7	2538.5	3504.8	3652.2
	E	1000.0	1163.8	1224.1	1454.0	1695.4	2196.4	2028.8	3143.7
	M	847.7	945.4	982.8	1163.8	1347.7	1775.9	2471.3	2548.5
			922.4	1066.1	1109.2	1313.2	1534.5	2002.9	2779.1
Methylamide of laevorotatory 2-(4'-methylbenzylsulphinyl) benzoic	E	948.3	1126.4	1178.2	1402.3	1620.7	2103.5	2879.3	2991.4
	M	977.0	1143.7	1201.2	1425.3	1649.4	2132.2	2896.6	3002.9

\* Solvent A = acetone, Ch = chloroform, D = dioxane, E = 96% ethanol, M = methanol.

Tab. 3. Molar rotations ( $M$ )<sub>570.1</sub><sup>20</sup> of p-bromophenacyl (1), p-nitrobenzyl (2) and methyl (3) esters of dextrorotatory 2-(4'-bromobenzylsulfinyl)benzoic, 2-(3'-bromobenzylsulfinyl)benzoic and 2-(4'-methylbenzylsulfinyl)benzoic acids

Compound	Methanol			Dioxane			Chloroform		
	1	2	3	1	2	3	1	2	3
2-(4'-Bromo-benzylsulfinyl)benzoic acid	1866.0	1622.0	1597.0	1909.1	1698.1	1610.8	1909.0	1574.8	1526.0
2-(3'-Bromo-benzylsulfinyl)benzoic acid	1534.0	-	1395.0	1522.9	1503.6	1303.4	1598.0	-	1303.4
2-(4'-Methyl benzylsulfinyl)benzoic acid	1456.6	1408.5	1352.4	1607.4	1531.3	1441.7	1569.7	1457.6	1372.5

Tab. 4. Effect of solvent on molar rotations ( $M$ )<sub>570.1</sub><sup>20</sup> of p-bromophenyl esters of dextrorotatory 2-(benzylsulfinyl)benzoic (1), 2-(4'-bromobenzylsulfinyl)benzoic (2) and 2-(4'-methylbenzylsulfinyl)benzoic (3) acids

Solvent	Compound		
	1	2	3
Dioxane	1482.1	1909.0	1607.4
Methanol	-	1866.0	1456.6
Ethanol	1400.0	1598.0	1447.1

a) in methanol:

$$(M)^{20} = \frac{3.7048659 \times 10^{11}}{\lambda^2 - (206.0)^2} - \frac{6.6479414 \times 10^{11}}{\lambda^2 - (212.0)^2} + \frac{3.7293748 \times 10^{11}}{\lambda^2 - (224.0)^2} - \frac{8.0775749 \times 10^{10}}{\lambda^2 - (242.0)^2} + \frac{2.4773188 \times 10^9}{\lambda^2 - (288.0)^2}$$

b) in acetone:

$$(M)^{20} = \frac{1.6408918 \times 10^{12}}{\lambda^2 - (206.0)^2} - \frac{2.9102485 \times 10^{12}}{\lambda^2 - (212.0)^2} + \frac{1.5921621 \times 10^{12}}{\lambda^2 - (224.0)^2} - \frac{3.3005392 \times 10^{11}}{\lambda^2 - (242.0)^2} + \frac{7.5999113 \times 10^9}{\lambda^2 - (288.0)^2}$$

c) in dioxane:

$$(M)^{20} = \frac{2.5770048 \times 10^{12}}{\lambda^2 - (206.0)^2} - \frac{4.5639299 \times 10^{12}}{\lambda^2 - (212.0)^2} + \frac{2.4891023 \times 10^{12}}{\lambda^2 - (224.0)^2}$$

Tab. 5. Effect of solvent on molar rotations  $(M)_{270.1}^{20}$  of methyl esters of 2-(benzylsulfinyl)benzoic (1), 2-(4'-bromobenzylsulfinyl)benzoic (2) and 2-(4'-methylbenzylsulfinyl)benzoic (3) acids

Solvent	Compound		
	1	2	3
Dioxane	1355.2	1611.0	1441.7
Methanol	1305.2	1597.0	1352.4
Ethanol	1223.5	1469.0	1326.4

$$-\frac{5.1311662 \times 10^{11}}{\lambda^2 - (242.0)^2} + \frac{1.1303429 \times 10^{10}}{\lambda^2 - (288.0)^2}$$

d) in chloroform:

$$(M)^{20} = \frac{1.0496794 \times 10^{12}}{\lambda^2 - (206.0)^2} - \frac{1.8830810 \times 10^{12}}{\lambda^2 - (212.0)^2} + \frac{1.0559751 \times 10^{12}}{\lambda^2 - (224.0)^2} - \frac{2.2843709 \times 10^{11}}{\lambda^2 - (242.0)^2} + \frac{6.1916889 \times 10^9}{\lambda^2 - (288.0)^2}$$

The values of molar rotations calculated by means of the above equations are given in brackets in Table 2.

The functions  $M(\lambda)$  describing in the rectangular system of coordinates (where  $\lambda$  is the independent variable) the optical properties of dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (10) have four extrema: two minima in the regions  $206 < \lambda < 212$  nm and  $224 < \lambda < 242$  nm and two maxima in the regions:  $212 < \lambda < 224$  nm and  $242 < \lambda < 288$  nm within the range  $0 < \lambda < 288$  nm. Their asymptotes are the  $\lambda$  axis and the straight lines perpendicular to it at points  $\lambda_1(206$  nm),  $\lambda_2(212$  nm),  $\lambda_3(224$  nm),  $\lambda_4(242$  nm) and  $\lambda_5(288$  nm).

In our further studies we have determined ( $200 < \lambda < 450$  nm) using methanol as solvent of the circular dichroism (CD) and the UV spectrum of laevorotatory enantiomer 8. The CD spectrum shows three negative maxima at  $\lambda = 206$ , 224 and 288 nm ( $(\theta)_{206} = -20846.8$ ,  $(\theta)_{224} = -61443.2$  and  $(\theta)_{288} = -46631.0$ ) as well two positive maxima at  $\lambda = 212$  and 242 nm ( $(\theta)_{212} = +9326.2$  and  $(\theta)_{242} = +19201.0$ ). The electronic spectrum shows in the region examined two absorption bands localized at  $\lambda = 212$  and 226 nm ( $\epsilon_{212} = 26263.3$  and  $\epsilon_{226} = 21438.8$ ).

Analysis of the results of optical measurements leads to a conclusion that the dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (10) shows within the spectral range examined three positive and two negative Cotton effects situated in the region  $\lambda = 206, 224, 228, 212$  and 242 nm.

The optical effects caused by introduction of methyl group to the para position of the benzene ring of benzyl group in the region of values for which optical rotatory dispersion is normal are not difficult to determine in spite of diverse solvent effects. Dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid 10 and its derivatives in all the solvents used in the measurements show molar rotations higher than

those of the corresponding unsubstituted with methyl group in the benzene ring compounds. The relative average percent increase of molar rotations ( $\% \Delta R_{mol}$ ) for free acid (10) is about 6.61%, 10.45% for its N-methylamide (12), 6.60% for methyl ester (11), 4.37% for p-bromophenacyl ester (13) and 4.66% for p-nitrobenzyl ester (14). Introduction of methyl group into the molecule of 2-(benzylsulfinyl)benzoic acid in the para position of the benzyl group increases the rotation of the system very considerably in spite of its high molar rotation. It is not excluded that this observation could be interpreted by the fact that the methyl groups attached to the benzene ring are disposing of an hyperconjugation effect influencing as it was observed earlier the optical properties of sulphoxide systems [16]. It should be also stressed that the compounds with bromine atom in the para position of the benzene ring of benzyl group [5,6,7] demonstrated the some optical effect.

Unambiguous interpretation of the observed phenomena requires further stereochemical studies.

## EXPERIMENTAL

The melting points are uncorrected. The polarimetric measurements were carried out by a Perkin - Elmer spectropolarimeter 241 MC using the solutions specified in the text. IR and UV spectra were determined by means of SP-200 and SP-700 spectrophotometers. CD spectra were obtained in a Jasco (model ORD(CD)) dichrograph. The compounds were examined as suspensions in Nujol (IR) and in solutions mentioned in the text.

### 1. 2-(4'-Methylbenzylthio)benzoic acid (1)

A sample of 9.25g (0.05 mole) of p-methylbenzyl bromide dissolved in 100 cm<sup>3</sup> of 96% ethanol was added in small portions with stirring to a warmed to 60° solution of 7.7g (0.05 mole) of thiosalicylic acid (colorless rods from acetic acid, m.p. 164-165°C, lit. [18] m.p. 164-165°C) in 50 cm<sup>3</sup> of 10% aqueous solution of NaHCO<sub>3</sub>. The mixture was stirred for 2 h, maintaining the temperature in the reactor at 50-60°C. The ethanol was distilled off under reduced pressure (12 mm Hg, water bath). The residue was filtered and acidified to Congo with dilute (1:1, V/V) HCl. A fine crystalline precipitate which soon separated, was filtered off, washed with water, dried in the air and crystallized from 96% ethanol (14g subst 200 cm<sup>3</sup> solv.). Colorless plates 10g, m.p. 192-193°C. The compound is readily soluble in acetone and chloroform, fairly soluble in methanol and 96% ethanol, and sparingly soluble in acetic acid.

#### Analysis:

For C<sub>15</sub>H<sub>14</sub>O<sub>2</sub>S (258.3) - Calcd.: 69.7%C, 5.4%H;  
found : 69.6%C, 5.6%H.

1. IR (cm<sup>-1</sup>): 750, 970 ( $\delta_{C_{Ar}-H}$ , subst. 1.2), 838 ( $\delta_{C_{Ar}-H}$ , subst. 1.4), 1030,



1050, 1120, 1210 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1460, 1520, 1570, 1590 ( $\nu C_{Ar}=C_{Ar}$ ), 710 ( $\nu C-S$ ), 900 ( $\delta OH$ ), 1260, 1280, 1390 ( $\delta OH$  i  $\nu C-O$ ), 1690 ( $\nu C=O$ , COOH).

### 2. Racemic 2-(4'-methylbenzylsulfinyl)benzoic acid (2)

A sample of 5.16g (0.02 mole) of powdered 2-(4'-methylbenzylthio)benzoic acid (1) was suspended in 50 cm<sup>3</sup> of glacial acetic acid. The suspension was warmed to 40°C, was added dropwise 2 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> (0.022 mole) and mechanically stirred for 2 h. Then the solution was cooled to room temperature and introduced to 200 cm<sup>3</sup> of water. A fine crystalline precipitate soon separated. It was filtered off, dried in the air and crystallized (4g) from benzene (700 cm<sup>3</sup>). Colorless needles (3g), m.p. 172°C (decomp.). The compound is readily soluble in methanol, 96% ethanol, acetone and acetic acid and sparingly soluble in benzene and cyclohexane.

Analysis:

For C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>S (274.3) - Calcd.: 65.7%C, 5.2%H, 11.7%S;  
found : 65.8%C, 5.4%H, 11.6%S.

1. IR (cm<sup>-1</sup>): 765 ( $\delta C_{Ar}-H$ , subst. 1.2), 860 ( $\delta C_{Ar}-H$ , subst. 1.4), 1060, 1110, 1170 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1480, 1525, 1600 ( $\nu C_{Ar}=C_{Ar}$ ), 700 ( $\nu C-S$ ), 1000 ( $\nu SO$ ), 890 ( $\delta OH$ ), 1250, 1270, 1390 ( $\delta OH$  i  $\nu C-O$ ), 1700 ( $\nu C=O$ , COOH).

### 3. Methyl ester of rac. 2-(4'-methylbenzylsulfinyl)benzoic acid (3)

To the suspension of 2.7g powdered rac. acid 2 in 20 cm<sup>3</sup> of dry ether cooled externally with ice and water the ether solution of diazomethane (100 cm<sup>3</sup>), prepared from 5g of N, N-nitrosomethyl urea [20], was added dropwise with stirring until permanent coloration of the liquid appeared. The mixture was refluxed (CaCl<sub>2</sub> tube) for 2 h. The solvent was distilled off under reduced pressure (12 mm Hg, water bath). The oily residue soon solidified. The crude product (2g, m.p. 100°C) was crystallized from heptane (60 cm<sup>3</sup>). Colorless needles (1.4g) m.p. 101-103°C. The compound is easily soluble in benzene, methanol, 96% ethanol and acetone and fairly soluble in hexane and heptane.

Analysis:

For C<sub>16</sub>H<sub>16</sub>O<sub>3</sub>S (288.3) - Calcd.: 66.6%C, 5.6%H;  
found : 66.5%C, 5.3%H.

### 4. N-Methylamide of rac. 2-(4'-methylbenzylsulfinyl)benzoic acid (4)

A sample of 1.45g powdered methyl ester 3 was suspended in 20 cm<sup>3</sup> of 40% methylamine solution and the suspension was mechanically shaken at room temperature for 24 h. The reaction product was filtered off, washed with water and after drying in the air, crystallized from a mixture of cyclohexane (25 cm<sup>3</sup>) and

benzene (35 cm<sup>3</sup>). Colorless plates (0.3g), m.p. 180°C. The compound is readily soluble in benzene, acetone, methanol and 96% ethanol and sparingly soluble in cyclohexane and petroleum ether.

Analysis:

For C<sub>16</sub>H<sub>17</sub>NO<sub>2</sub>S (287.4) - Calcd.: 66.9%C, 6.0%H, 4.9%N;  
found : 66.6%C, 5.8%H, 4.6%N.

5. *p*-Bromophenacyl ester of rac. 2-(4'-methylbenzylsulfinyl)benzoic acid (5)

Rac. acid 2 (1.37g, 0.005 mole) and *p*-bromophenacyl bromide (1.38g, 0.005 mole) were used in the esterification reaction which was carried out for 1h. in 110 cm<sup>3</sup> of boiling 91% methanol. The reaction product was filtered off (1.2g, m.p. 169-170°C) and crystallized from methanol (120 cm<sup>3</sup>). Colorless needles (1g), m.p. 172-173°C. The compound is readily soluble in benzene and chloroform, fairly soluble in acetone and 96% ethanol and sparingly soluble in cyclohexane.

Analysis:

For C<sub>23</sub>H<sub>19</sub>BrO<sub>4</sub>S (471.4) - Calcd.: 58.6%C, 4.1%H;  
found : 58.3%C, 4.2%H.

6. *p*-Nitrobenzyl ester of rac. 2-(4'-methylbenzylsulfinyl)benzoic acid (6)

Rac. acid 2 (1.37g, 0.005 mole) and *p*-nitrobenzyl bromide (1.1g, 0.005 mole) were used in esterification which was carried out for 1h. in 90 cm<sup>3</sup> of 90% boiling methanol. The reaction product was filtered off, washed with water, dried in the air (1.3g, m.p. 148-150°C) and crystallized from methanol (70 cm<sup>3</sup>). Colorless needles (0.9g), m.p. 149-150°C. The compound is readily soluble in benzene and chloroform, fairly soluble in acetone and 96% ethanol and sparingly soluble in cyclohexane.

Analysis:

For C<sub>22</sub>H<sub>19</sub>NO<sub>5</sub>S (409.4) - Calcd.: 64.5%C, 4.7%H, 3.4%N;  
found : 64.3%C, 4.8%H, 3.4%N.

7. *Brucine salt of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (7)*

A sample of 5.5g (0.02 mole) of rac. acid 2 was mixed with 7.9g (0.02 mole) of powdered brucine and the mixture was dissolved in 100 cm<sup>3</sup> of boiling acetone. The hot solution was filtered and was left standing at room temperature for crystallization. After 24 h the first fraction of the salt was filtered off. Colorless needles (5.1g), m.p. 175°C (decomp.), ( $\alpha$ )<sub>D</sub><sup>20</sup> = -148.0° (c=0.5, d=2,  $\alpha$  = -1.48°) in 96% ethanol. After two crystallizations of the first fraction from acetone (I: 13.4g, 100 cm<sup>3</sup>, 5.1g, -148.0°, 175°C; II: 5.1, 580, 2.8, -196.0, 178; III: 2.8, 300, 1.8, -196.0, 178) the product exhibited physical properties

which remained unchanged by further crystallization. Colorless needles (1.8g), m.p. 178°C (decomp.) ( $\alpha$ )<sub>D</sub><sup>20</sup> = -196.0° (c=0.5, d=2,  $\alpha$  = -1.96°) in 96% ethanol. The brucine salt of laevorotatory enantiomer is easily soluble in benzene and chloroform, fairly soluble in acetone and 96% ethanol and sparingly soluble in cyclohexane.

Analysis:

For C<sub>38</sub>H<sub>42</sub>N<sub>2</sub>O<sub>7</sub>S (668.7) - Calcd.: 4.2%N;  
found : 4.3%N.

### 8. Laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (8)

Brucine salt 7 (1.8g) was suspended in 10 cm<sup>3</sup> of water. The suspension was stirred and was carefully acidified with 10 cm<sup>3</sup> of 3% HCl. The resulting acid 8 was filtered off and was immediately dissolved in 20 cm<sup>3</sup> of 3% NaOH. The solution was filtered and was extracted (3x20 cm<sup>3</sup>) with chloroform. The alkaline liquid was acidified (Congo) with 3% HCl after removing the dissolved chloroform by distillation under reduced pressure (12 mmHg, water bath temp. 45°C). The laevorotatory acid separated immediately in the form of crystalline precipitate. It was filtered off, washed with water, dried (0.7g, m.p. 172-173°C with decomp., ( $\alpha$ )<sub>D</sub><sup>20</sup> = -450.0°) and then crystallized from benzene (100 cm<sup>3</sup>). Colorless needles (0.5g), m.p. 172-173°C (decomp.), ( $\alpha$ )<sub>D</sub><sup>20</sup> = -480.0° (c=0.1, d=0.5,  $\alpha$  = -0.240°) in 96% ethanol. The acid is readily soluble in acetone and 96% ethanol, fairly soluble in benzene and chloroform and sparingly soluble in cyclohexane.

Analysis:

For C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>S (274.3) - Calcd.: 65.7%C, 5.1%H;  
found : 65.5%C, 5.0%H.

### 9. Strychnine salt of dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (9)

The mother liquors from the first fraction of brucine salt of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (p.7) were evaporated under reduced pressure (12 mm Hg, water bath temp. 40°C) to dryness. The obtained salt was converted into free acid (4.5g, m.p. 161-163°C (decomp.), ( $\alpha$ )<sub>D</sub><sup>20</sup> = +335.0° in 96% ethanol) as in section 8. 4.5g (0.016 mole) of this acid was mixed with 5.1g (0.016 mole) of strychnine and the mixture was dissolved in 30 cm<sup>3</sup> of boiling 96% ethanol. The hot solution was filtered and was left standing at room temperature for crystallization. After 24 h the first fraction was filtered off. Colorless needles (6.3g), m.p. 221-222°C, ( $\alpha$ )<sub>D</sub><sup>20</sup> = +183.0°, (c=0.5, d=2,  $\alpha$  = +1.83°) in 96% ethanol. After recrystallization of the first fraction (6.2g) from 70% ethanol (20 cm<sup>3</sup>) the salt had physical properties which remained unchanged by further crystallization. Colorless needles (4g), m.p. 221-222°C, ( $\alpha$ )<sub>D</sub><sup>20</sup> = +183.0° (c=0.5, d=2,  $\alpha$  = +1.83°) in 96% ethanol. The salt is readily soluble in benzene, chloroform and 96% ethanol and very sparingly soluble in water.

## Analysis:

For  $C_{36}H_{35}N_2O_5S$  (608.7) - Calcd.: 4.6%N;  
found : 4.4%N.

## 10. Dextrorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (10)

Strychnine salt **9** (4g, m.p. 221-222°C,  $(\alpha)_D^{20} = +183.0^\circ$  in 96% ethanol) was converted into free acid as in section 8. Crude acid (1.8g) m.p. 172-173°C, (decomp.),  $(\alpha)_D^{20} = +460.0^\circ$  in 96% ethanol) was crystallized from benzene (300 cm<sup>3</sup>). Colorless needles (1.5g), m.p. 172-173°C (decomp.),  $(\alpha)_D^{20} = +480.0^\circ$  (c=0.1, d=0.5,  $\alpha = +0.240^\circ$ ) in 96% ethanol. The compound is readily soluble in acetone, methanol and 96% ethanol, fairly soluble in benzene and sparingly in cyclohexane.

## Analysis:

For  $C_{15}H_{14}O_3S$  (274.3) - Calcd.: 65.7%C, 5.1%H, 11.7%S;  
found : 65.7%C, 5.3%H, 11.7%S.

IR (cm<sup>-1</sup>): 750 ( $\delta C_{Ar}-H$ , subst. 1.2), 820 ( $\delta C_{Ar}-H$ , subst. 1.4), 1050, 1100, 1235 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1465, 1520, 1570, 1590 ( $\nu C_{Ar}=C_{Ar}$ ), 690 ( $\nu C-S$ ), 995 ( $\nu SO$ ), 880 ( $\delta OH$ ), 1260, 1290, 1400 ( $\delta OH$  i  $\nu C-O$ ), 1685 ( $\nu C=O$ , COOH).

## 11. Methyl ester of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (11)

1.3g of laevorotatory acid **8** was converted into its methyl ester as in section 3. The transformation product (1.2g m.p. 93-94°C  $(\alpha)_D^{20} = -430.0^\circ$  in 96% ethanol) was crystallized from heptane (35 cm<sup>3</sup>). Colorless needles (0.9g), m.p. 93-94°C,  $(\alpha)_D^{20} = -435.0^\circ$  (c=0.1, d=0.5,  $\alpha = -0.2175^\circ$ ) in 96% ethanol. The compound is readily soluble in benzene, acetone and 96% ethanol, fairly soluble in heptane and cyclohexane.

## Analysis:

For  $C_{16}H_{16}O_3S$  (288.3) - Calcd.: 66.6%C, 5.6%H;  
found : 66.9%C, 5.6%H.

## 12. N-Methylamide of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (12)

Methyl ester (1.4g) **11** was converted into the corresponding methylamide as in section 4. The product (0.8 m.p. 179-180°C,  $(\alpha)_D^{20} = -390.0^\circ$  in 96% ethanol) was crystallized from the mixture of benzene (70 cm<sup>3</sup>) and cyclohexane (50 cm<sup>3</sup>). Colorless plates (0.5g), m.p. 179-180°C,  $(\alpha)_D^{20} = -392.0^\circ$  (c=0.1, d=0.5,  $\alpha = -0.196^\circ$ ) in 96% ethanol. The compound is readily soluble in benzene, acetone and 96% ethanol and sparingly soluble in heptane and cyclohexane.

## Analysis:

For  $C_{16}H_{17}NO_2S$  (287.4) - Calcd.: 66.9%C, 6.0%H, 4.8%N;  
found : 66.7%C, 6.1%H, 4.8%N.

13. *p*-Bromophenacyl ester of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (13)

Laevorotatory acid 8 (1.37g, 0.005 mole) and *p*-bromophenacyl bromide (1.38g, 0.005 mole) were used in esterification reaction which was carried out for 1 h in 110 cm<sup>3</sup> of boiling 91% methanol. The reaction product was filtered off, washed with water, air dried (1.6g, m.p. 176-177°C,  $(\alpha)_D^{20} = -292.0^\circ$  in 96% ethanol) and crystallized from methanol (170 cm<sup>3</sup>). Colorless needles (1.2g) m.p. 176-177°C,  $(\alpha)_D^{20} = -292.0^\circ$  (c=0.1, d=0.5,  $\alpha = -0.146^\circ$ ) in 96% ethanol. The compound is easily soluble in chloroform and acetone, fairly soluble in 96% ethanol and sparingly soluble in cyclohexane.

## Analysis:

For  $C_{23}H_{19}BrO_4S$  (471.4) - Calcd.: 58.6%C, 4.1%H;  
found : 58.3%C, 4.2%H.

14. *p*-Nitrobenzyl ester of laevorotatory 2-(4'-methylbenzylsulfinyl)benzoic acid (14)

Acid 8 (1.37g, 0.005 mole) and *p*-nitrobenzyl bromide (1.1g, 0.005 mole) were used in esterification reaction. The reaction was carried out 1 h in boiling 90% methanol (45 cm<sup>3</sup>). The separated from post reaction solution precipitate was filtered off, washed with water (3 cm<sup>3</sup>), air dried (1.4g, m.p. 139-141 °C,  $(\alpha)_D^{20} = -300.0^\circ$  (c=0.1, d=0.5  $\alpha = -0.150^\circ$ ) in 96% ethanol) and crystallized from methanol (30 cm<sup>3</sup>) colorless needles (1g), m.p. 141-143°C,  $(\alpha)_D^{20} = -312.0^\circ$  (c=0.1, d=0.5,  $\alpha = -0.156^\circ$ ) in 96% ethanol. The ester is easily soluble in chloroform and acetone fairly soluble in methanol and 96% ethanol and sparingly in cyclohexane.

## Analysis:

For  $C_{22}H_{19}NO_5S$  (409.4) - Calcd.: 64.5%C, 4.9%H, 3.4%N;  
found : 64.5%C, 4.8%H, 3.4%N.

15. 2-(4'-methylbenzylsulfonyl)benzoic acid (15)

A suspension of 1.28g of acid 1 in 30 cm<sup>3</sup> of glacial acetic acid was treated with 10 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> and was heated 1 h on water bath. The post-reaction solution was poured in 150 cm<sup>3</sup> of water. A fine crystalline precipitate separated. It was filtered off, dried in the air (1g, m.p. 182-184°C) and then crystallized from benzene (60 cm<sup>3</sup>). Colorless needles (0.8g) m.p. 183-184°C. The acid is easily soluble

in chloroform, acetone and 96% ethanol, fairly soluble in benzene and sparingly soluble in cyclohexane.

Analysis:

For  $C_{15}H_{14}O_4S$  (296.3) - Calcd.: 62.1%C, 4.9%H, 11.3%S;  
found : 62.3%C, 4.7%H, 11.0%S.

IR ( $cm^{-1}$ ): 770, 958 ( $\delta C_{Ar}-H$ , subst. 1.2), 838 ( $\delta C_{Ar}-H$ , subst. 1.4), 1060, 1122 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1460, 1500, 1580, 1600 ( $\nu C_{Ar}=C_{Ar}$ ), 690 ( $\nu C-S$ ), 1156 ( $\nu S SO_2$ ), 1310 ( $\nu as SO_2$ ), 910 ( $\delta OH$ ), 1220, 1280, 1390 ( $\delta OH$  i  $\nu C-O$ ), 1705 ( $\nu C=O$ , COOH).

#### 16. Rac. 3-(4'-methylphenyl)-4-thiaisochroman-1-one (16)

Rac. acid 2 (1.37g) was suspended in 25  $cm^3$  of acetic acid anhydride and heated on water bath under reflux condenser ( $CaCl_2$  tube) for 2 h. The post-reaction solution was cooled to 15°C and introduced to water (100  $cm^3$ ). A fine crystalline precipitate soon separated. It was filtered off and was dissolved in benzene (150  $cm^3$ ). The benzene solution was extracted with 10%  $NaHCO_3$  (2 x 25  $cm^3$ ), washed with water (2 x 25  $cm^3$ ) and dried with anhydrous  $MgSO_4$ . The solvent was removed by distillation under reduced pressure (12 mm Hg, water bath). The residue was crystallized from 96% ethanol (20  $cm^3$ ). Colorless rods (0.6g), m.p. 125-126°C. The compound is easily soluble in benzene and ether, fairly soluble in acetone and 96% ethanol and sparingly soluble in petroleum ether and cyclohexane.

Analysis:

For  $C_{15}H_{12}O_2S$  (256.3) - Calcd.: 70.3%C, 4.7%H;  
found : 70.5%C, 4.9%H.

IR ( $cm^{-1}$ ): 755, 1000 ( $\delta C_{Ar}-H$ , subst. 1.2), 840 ( $\delta C_{Ar}-H$ , subst. 1.4), 1025, 1050, 1100, 1220 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1460, 1515, 1590, 1610 ( $\nu C_{Ar}=C_{Ar}$ ), 680 ( $\nu C-S$ ), 1250, 1280, ( $\nu C-O$ ,  $\delta$  lactone), 1720 ( $C=O$ ,  $\delta$  lactone).

#### 17. Laevorotatory 4-(4'-methylphenyl)-4-thiaisochroman-1-one (17)

To a solution of 1g of laevorotatory acid 8 in 25  $cm^3$  of benzene 7  $cm^3$  of acetic anhydride was added and the mixture was then refluxed ( $CaCl_2$  tube) for 2 h. The cooled post reaction solution was extracted with 10%  $NaHCO_3$  (2 x 30  $cm^3$ ), washed with water (2 x 50  $cm^3$ ) and dried with anhydrous  $MgSO_4$ . The solvent was removed by distillation under reduced pressure (12 mm Hg, water bath). The residue (0.5g, m.p. 117-124°C,  $(\alpha)_D^{20} = -17.0^\circ$  in 96% ethanol) was crystallized from 96% ethanol (15  $cm^3$ ). Colorless rods (0.4g), m.p. 127-129°C,  $(\alpha)_D^{20} = -10.0^\circ$  ( $c=0.2$ ,  $d=0.5$ ,  $\alpha=-0.01^\circ$ ) in 96% ethanol. The compound is easily soluble in benzene, acetone and 96% ethanol sparingly soluble in cyclohexane.

Analysis:

For  $C_{15}H_{12}O_2S$  (256.3) - Calcd.: 70.3%C, 4.7%H;  
found : 70.4%C, 4.9%H.

IR ( $cm^{-1}$ ): 760, 1000 ( $\delta C_{Ar}-H$ , subst. 1.2), 840 ( $\delta C_{Ar}-H$ , subst. 1.4), 1030, 1050, 1100, 1220 ( $\delta C_{Ar}-H$ , subst. 1.2 i 1.4), 1470, 1510, 1590 ( $\nu C_{Ar}=C_{Ar}$ ), 680 ( $\nu C-S$ ), 1180, 1255, ( $\nu C-O$ ,  $\delta$  lactone), 1720 ( $\nu C=O$ ,  $\delta$  lactone/).

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Functions (M) ( $\lambda$ ) have been determined by St. Grzegórski, Ph. D., Institute of Mathematics. M. Curie-Skłodowska University.

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## STRESZCZENIE

Opisano syntezę i podstawowe właściwości kwasów 2-(4'-metylobenzosulfinylo)- i 2-/4'-metylobenzosulfonylo/benzoesowych. Racemiczny sulfotlenek rozszczepiono w drodze krystalizacji frakcyjnej obojętnych soli z brucyną i strychniną na enancjomery. Na podstawie przeprowadzonych badań korelacyjnych przypisano poszczególnym enancjomerom bezwzględne konfiguracje. Zdefiniowano w rejonie  $400 \leq \lambda \leq 623.4$  nm dyspersję optycznej rotacji prawoskrętnego enancjomeru oraz jego pochodnej metyloamidowej i pochodnych estrowych. Wyznaczono pięciocłonowe równania opisujące rotację optyczną prawoskrętnego enancjomeru w badanym zakresie widmowym. Określono metodami kinetyki klasycznej stałe racemizacji (K) oraz parametry aktywacji ( $E_a$ ,  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$ ) dla procesu racemizacji prawoskrętnego kwasu 2-(4'-metylobenzosulfinylo)benzoesowego. Wykonano przegrupowania racemicznego i lewoskrętnego kwasu 2-(4'-metylobenzosulfinylo)benzoesowego do racemicznego i lewoskrętnego 3-(4'-metylofenylo)-4-tiaizochroman-1-onu.

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