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**The Effect of Molecular Structure on the Optical Properties of Sulfoxide Systems.
2-(3'-bromobenzylsulfinyl)-benzoic Acids and Some of Their Derivatives. IV^{*}, ****

Wpływ budowy cząsteczkowej na własności optyczne układów sulfotlenkowych.
Kwasy 2-(3'-bromobenzylsulfinylo)-benzoesowe i ich niektóre pochodne. IV

Влияние молекулярного строения на оптические свойства сульфокислых систем.
Кислоты 2-(3'-бромбензилсульфинил)-бензойные и некоторые их производные. IV

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 example of benzylsulfinylacetic acids and their derivatives. The observed optical order in the group of isomeric

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^{XX} Part III: Kozioł A., Majewski W., Janczewski M., Acta Cryst., in press.

bromobenzylsulfinylacetic acids [1-4] as well as in the group of isomeric methylbenzylsulfinylacetic acids [5] suggested that a single methylene group does not isolate completely the sulfoxide system from the effects caused by introduction of substituents to aromatic ring. The observed optical and stereochemical relationships encouraged us to further studies in the group of benzylsulfinylbenzoic acids and their homologues. 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 chiroptical properties of 2-(benzylsulfinyl)-benzoic acids and their bromo derivatives with halogen atom in the benzene ring of benzyl group i.e. isomeric 2-(bromobenzylsulfinyl)-benzoic acids. As a reference system having the character of configurational standard as well as a standard for comparing the measured rotation values we assumed unsubstituted 2-(benzylsulfinyl)-benzoic acid arbitrarily assigning the R [6] configuration to dextrorotatory enantiomer.

In the previous papers [6,7] the synthesis and some chiroptical properties of enantiomeric 2-(benzylsulfinyl)-benzoic acids and their 4'-bromoderivatives were described.

In the present communication we are reporting the synthesis and the determination of principal optical and stereochemical properties of enantiomeric 2-(3'-bromobenzylsulfinyl)-benzoic acids.

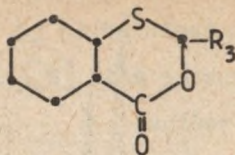
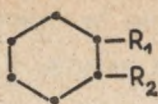


Fig. 1. Structural patterns

- | | |
|---|---|
| <u>1</u> : $R_1 = S \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = COOH$ |
| <u>2</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = COOH$ |
| <u>3</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = CO \cdot OCH_3$ |
| <u>4</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = CO \cdot NHCH_3$ |
| <u>5</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4 \cdot Br$ |
| <u>6</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($-$) | $R_2 = CO \cdot OCH_2 \cdot C_6H_4 \cdot NO_2$ |
| <u>7</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($-$) | $R_2 = COOH \cdot Bruc.$ |
| <u>8</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = COOH$ |
| <u>9</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = COOH \cdot Bruc.$ |
| <u>10</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = COOH$ |
| <u>11</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = CO \cdot OCH_3$ |
| <u>12</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = CO \cdot NHCH_3$ |
| <u>13</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4 \cdot Br$ |
| <u>14</u> : $R_1 = SO \cdot CH_2 \cdot C_6H_4 \cdot Br,$
($+$) | $R_2 = CO \cdot OCH_2 \cdot C_6H_4 \cdot NO_2$ |
| <u>15</u> : $R_1 = SO_2 \cdot CH_2 \cdot C_6H_4 \cdot Br,$
(\pm) | $R_2 = COOH$ |
| <u>16</u> : $R_3 = CH \cdot C_6H_4 \cdot Br,$ | ($+$) |
| | <u>17</u> : $R = CH \cdot C_6H_4 \cdot Br$ |

The starting material in our studies was 2-(3'-bromobenzyl-mercapto)-benzoic acid (1), which was obtained by coupling 2-mercaptobenzoic acid [8] with m-bromobenzyl bromide [4,9] in alkaline medium.

Racemic 2-(3'-bromobenzylsulfinyl)-benzoic acid (2) was obtained by oxidation of the compound 1 with 30% hydrogen peroxide in glacial acetic acid. When mercapto 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 acid 2 was resolved by crystallization of diastereomeric salts with brucine. Optically active 2-(3'-bromobenzylsulfinyl)-benzoic acids (8 and 10) separated from the alkaloid salts and purified from diluted ethanol showed a high specific rotation ($[\alpha]_D^{20} = -355,0^\circ, 360,0^\circ$ (ethanol).

The optical purity of enantiomeric 2-(3'-bromobenzylsulfinyl)-benzoic acids 8 and 10 was confirmed by comparative studies of the $^1\text{H NMR}$ spectra of racemic acid 2 (Fig. 2 a) and laevorotatory enantiomer 8 (Fig. 2 b) methyl ester mixtures with tris-(3-trifluoroacetyl-d-camphorato)-europium (III) ($\text{Eu}(\text{tfc})_3$) as a chiral shift reagent.

The presented fragment of $^1\text{H NMR}$ spectrum of racemic acid methyl ester mixture (Fig. 2a) with a chiral shift reagent demonstrates diastereomeric differentiation (two AB quartets) of methylene group protons. On the other hand on the spectrum (Fig. 2b) of laevorotatory 2-(3'-bromobenzylsulfinyl)-benzoic



Fig. 2a

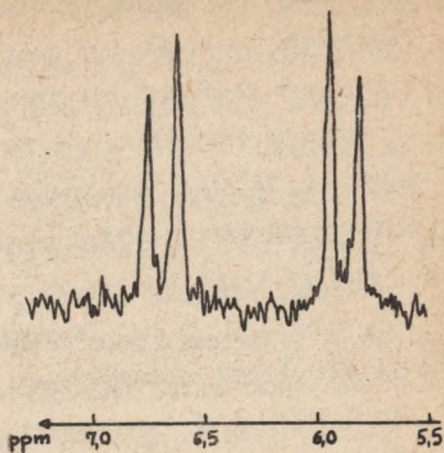


Fig. 2b

Fig. 2. a - Methylene groups protons ^1H NMR spectrum of the mixture of racemic 2- 3'-bromobenzylsulfinyl -benzoic acid methyl ester and tris- 3-trifluoroacetyl-d-camphorato - europium III 22:20 mg, b - Methylene groups protons ^1H NMR spectrum of the mixture of dextrorotatory 2- 3'-benzylsulfinyl -benzoic acid methyl ester and tris- 3-trifluoroacetyl-d-camphorato - europium III 21:20 mg

acid methyl ester mixture with $\text{Eu}(\text{tfc})_3$ realized under the same conditions this effect is not observable (only one AB quartet). That proves enantiomeric 2-(3'-bromobenzylsulfinyl) -benzoic acids being optically pure in the range of accuracy (2-3%) of the applied ^1H NMR method.

Mixing of antipodes 8 and 10 in equimolar proportion. followed by crystallization caused the regeneration of racemic acid 2. The melting point of the racemate 2 is considerably lower ($t = 24^\circ\text{C}$) than that of the antipodes 8 and 10. The IR spectrum of racemic acid 2 was not different in the finger print region from the spectra of enantiomers 8 and 10.

The relatively easy resolution of optically inactive compound 2 into enantiomers (8 and 10) and the physical properties quoted above indicate that racemic acid 2 belongs to the type of racemic mixture.

Optically active 2-(3'-bromobenzylsulfinyl)-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 were studied using a mixture (2:1 v/v) of dioxane and dilute (2,5:1, v/v, HCl:H₂O) hydrochloric acid as solvent. Under these conditions the racemization of optically active acids 8 and 10 obeyed the kinetic equation of the first order reactions ($K = \frac{1}{t} \ln \frac{\alpha_0}{\alpha}$). The racemization constants (K), the activation entropies (ΔS^\ddagger) and the activation enthalpies (ΔH^\ddagger) calculated for three temperatures after averaging the kinetic measurements by the last squares method, are shown in Tab. 1. The activation parameters of the racemization processes have been determined by the classical kinetic methods on the basis of the Eyring equation [10].

Tab. 1.

Thermodynamic characterization of racemization of the optically active 2-(3'-bromobenzylsulfinyl)-benzoic acids

Racemization temperature t , °C	Racemization constants $K \times 10^5$ sek ⁻¹	Activation entropy ΔS^\ddagger , eu	Activation enthalpy ΔH^\ddagger Kcal/mol, KJ/mol
13	19,63 ± 1,45	-3,40 ± 0,29	20,60 [±] 0,04 86,23 [±] 0,17
15	25,22 ± 2,00	-3,41 ± 0,32	20,60 [±] 0,04 86,23 [±] 0,17
17	32,82 ± 1,36	-3,43 ± 0,16	20,59 [±] 0,02 86,19 [±] 0,08

The activation energy (E_a) and the preexponential factor ($A = K_{\max}$) have been determined from the empirical Arrhenius equation: ($K = A \times e^{-E_a/RT}$) $E_a = 21,170$ Kcal/mol, $A = 2949 \times 10^9 \text{ sec}^{-1}$. The negative values of the activation entropy ($\Delta S^\ddagger < 0$) indicate that in the transition state of the racemization process additive compounds or intermediates previously proposed for arylalkylsulfoxides by German [11,12,13] and American [14,15] authors, are formed.

Rac. 2-(3'-bromobenzylsulfinyl)-benzoic acid (2) according to expectations [16] have been transformed by heating with acetic anhydride into optically inactive 3-(3'-bromophenyl)-4-thia-isochroman-1-one (16). The structure of 3-(3'-bromophenyl)-4-thia-isochroman-1-one (16) was confirmed by elemental analysis and spectral methods (the IR spectra are shown in the Experimental Part). In order to know if bromine atom in the benzene ring of the benzylgroup can have some influence on stereochemical course of the rearrangement reaction we have transformed by using acetic anhydride under the same conditions dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid. On this way we have obtained dextrorotatory 3-(3'-bromophenyl)-4-thia-isochroman-1-one (17), $(\alpha)_D^{20} = +6,5^\circ$ (in 96% ethanol), with 58% yield and 8% optical purity. The optical purity of the rearrangement product was determined by studying the $^1\text{HNMR}$ spectra of methine group protons in diastereomeric compounds formed with tris-(3-trifluoroacetyl-d-camphorato)-europium (III) ($\text{Eu}(\text{tfc})_3$) using deuteriochloroform as solvent.

Taking into account the previously obtained results by rearrangement of unsubstituted laevorotatory 2-(benzylsulfinyl) [6] and laevorotatory 2-(4'-bromobenzylsulfinyl)-benzoic acids [7] it is possible to observe that the introduction of



Fig. 3. Methine groups protons ^1H NMR spectrum of the mixture of dextrorotatory 3-3'-bromophenyl -4-thiaisochroman-1-one and tris-3-trifluoroacetyl-d-camphorato - europium III

20:50 mg

bromine atom into the molecule of 2-(benzylsulfinyl)-benzoic acid in the meta position of the benzene ring of benzyl group considerably decreases both the yield and the optical purity of the rearrangement product. It is not excluded that our observations could be interpreted on the ground of the rearrangement mechanism proposed by Oae and Numata [17]. Accumulating a larger number of experimental data will give the possibility to draw more general conclusions.

Tab. 2

Rotatory dispersion of dextrorotatory 2-/3'-bromobenzylsulfinyl/ -benzoic acid and some of its derivatives

Compound	Solvent	Molar rotation /M/20						
		=589,3 nm	=579,1 nm	=546,1 nm	=520,0 nm	=480,0 nm	=440,0 nm	=435,8 nm
Dextrorotatory 2-/3'-bromobenzyl- sulfinyl/-benzoic acid	A	1347 /1349/	1418 /1419/	1676 /1690/	1957 /1969/	2571 /2574/	3582 /3574/	3725 /3718/
	Ch	1181 /119/	1235 /1257/	1457 /1493/	1689 /1738/	2252 /2278/	3182 /3199/	3311 /3333/
	D	118 /119/	1245 /1255/	1479 /1491/	1730 /1736/	2296 /2282/	3243 /3220/	3375 /3359/
	E	117 /117/	1228 /1232/	1448 /1466/	1693 /1706/	2222 /2224/	3080 /3071/	3202 /3192/
	M	1211 /1216/	1279 /1278/	1503 /1518/	1754 /1764/	2293 /2296/	3175 /3165/	3301 /3288/
Methyl ester of dextrorotatory 2-/3'-bromobenzyl- sulfinyl/ -benzoic acid	A	1314	1374	1639	1911	2512	3511	3649
	Ch	1240	1303	1551	1809	2356	3370	3508
	D	1247	1303	1551	1812	2395	3010	3508
	E	1194	1251	1491	1738	2289	3200	-
	M	1332	1395	1646	1925	2515	3469	3610
Methyl amide of dextrorotatory 2-/3'-bromobenzyl- sulfinyl/-benzoic acid	A	1187	1247	1472	1719	2262	3142	3269
	Ch	824	853	1043	1205	1606	2272	2367
	D	888	937	1117	1317	1758	2483	2582
	E	1029	1078	1272	1480	1944	2705	2811
	M	1089	1177	1360	1575	2057	2677	2931
p-Bromophenacyl ester of dextrorotatory 2-/3'-bromobenzyl- sulfinyl/-benzoic acid	A	1673	1738	2027	2349	3078	4301	4472
	Ch	1544	1598	1834	2113	2789	3915	4043
	D	1459	1523	1791	2102	2799	3990	4151
	E	1469	1534	1770	2049	2692	3765	3904
	M	1459	1534	1780	2070	2713	3786	3947
p-Nitrobenzyl ester of dextrorotatory 2-/3'-bromobenzyl- sulfinyl/-benzoic acid	A	1613	1698	2011	2334	3064	4269	4449
	D	1433	1504	1779	2087	2770	3923	4089
	E	1347	1423	1679	1964	2580	3595	3738
	M	1480	1546	1840	2135	2799	3852	4003

Solvent: A=acetone, Ch=chloroform, D=dioxane, E=ethanol, M=methanol.

In order to obtain a larger comparative material for chiroptical studies we have prepared the following derivatives of dextrorotatory acid 10: methylamide 12 and methyl ester 11, p-bromophenacyl ester 13 and p-nitrobenzyl ester 14. The mild conditions in which the reaction were carried out were not likely to cause racemization at the asymmetric sulfur atom. The molar rotations of dextrorotatory acid 10 and its derivatives 11, 12, 13 and 14 were determined in spectral region $350 \leq \lambda \leq 623,4$ nm using methanol (M), 96% ethanol (E), acetone (A), chloroform (Ch) and dioxane (D) as solvents. The results of measurements are shown in Tab. 2.

As it appears from the comparison of the numerical values given in this table, the nature of the solvent has not considerable effect on the value of molar rotation. In the visible part of the spectrum the absolute values of molar rotations in the examined solvents decrease in the following order:

a) free acid: $A > E > D > Ch > M$; b) acid methylamide: $A > M > E > D > Ch$; c) methyl ester: $M > A > D > Ch > E$; d) p-bromophenacyl ester: $A > Ch > E > M > D$ and e) p-nitrobenzyl ester: $A > M > D > E$.

Analysis of the numerical data summarized in Table 2 shows that the curves representing function $\frac{1}{\lambda}(\lambda)^2$ in the region $435 < \lambda < 623,4$ nm for dextrorotatory acid 10 and its derivatives 11, 12, 13 and 14 are almost straight lines, which leads to the conclusion that the optical rotatory dispersion of the compounds examined (in the visible part of the spectrum) has the character of normal dispersion.

Comparison of the Freudenberg optical shifts presented in Table 3 and molar rotation changes caused by changes in the character of solvent which are summarized in Table 4 indicates

Tab. 3

Molar rotations (M_D^{20}) of p-bromophenacyl (1), p-nitrobenzyl (2) and methyl (3) esters of dextrorotatory 2-(4'-bromobenzylsulfinyl)-benzoic and 2-(3'-bromobenzylsulfinyl)-benzoic acids

	Ethanol			Acetone			Dioxane			Chloroform		
	1	2	3	1	2	3	1	2	3	1	2	3
2-(4'-bromobenzylsulfinyl)-benzoic acid	1598,0	-	1469,5	2091,4	1764,5	1596,6	1909,1	1698,1	1610,8	1909,0	1574,8	1526,0
2-(3'-bromobenzylsulfinyl)-benzoic acid	1533,7	1423,0	1250,5	1737,5	1698,1	1374,1	1522,9	1503,6	1303,4	1598,0	-	1303,4

Tab. 4

Effect of solvent on molar rotations (M)_{589,3}²⁰ of dextrorotatory 2-(4'-bromobenzylsulfanyl)-benzoic and 2-(3'-bromobenzylsulfanyl)-benzoic acids and their p-nitrobenzyl as well as methyl esters

Solvent	2-(4'-Bromobenzylsulfanyl)-benzoic acid	2-(3'-Bromobenzylsulfanyl)-benzoic acid	p-Nitrobenzyl ester of 2-(4'-bromobenzylsulfanyl)-benzoic acid	p-Nitrobenzyl ester of 2-(3'-bromobenzylsulfanyl)-benzoic acid	Methyl ester of 2-(4'-bromobenzylsulfanyl)-benzoic acid	Methyl ester of 2-(3'-bromobenzylsulfanyl)-benzoic acid
Acetone	1526,5	1346,7	1415,6	1612,7	1525,9	1314,0
Dioxane	1465,4	1183,8	1360,2	1432,5	1526,0	1246,9
Ethanol	1411,1	1173,7	1273,0	1347,1	1398,8	1193,9

that spatial configuration of dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid is R (+).

Our configuration standard was dextrorotatory 2-(4'-bromobenzylsulfinyl)-benzoic acid which spatial structure was determined by the X-ray structural analysis [18] as R (+).

On the basis of the numerical data ($340 < \lambda < 623,4$ nm) summarized in Table 2 functions (M) (λ) have been calculated for dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid. These functions have the character of the following four-term equations:

a) in methanol:

$$(\alpha)_\lambda^{20} = \frac{2.4855163 \times 10^9}{\lambda^2 - (215,0)^2} - \frac{2.8240969 \times 10^9}{\lambda^2 - (245,0)^2} + \frac{1.0973607 \times 10^9}{\lambda^2 - (287,0)^2} - \frac{4.6920609 \times 10^8}{\lambda^2}$$

b) in ethanol:

$$(\alpha)_\lambda^{20} = \frac{3.5639914 \times 10^9}{\lambda^2 - (215,0)^2} - \frac{3.8559243 \times 10^9}{\lambda^2 - (245,0)^2} + \frac{1.2660735 \times 10^9}{\lambda^2 - (287,0)^2} - \frac{7.0227594 \times 10^8}{\lambda^2}$$

c) in acetone:

$$(\alpha)_\lambda^{20} = \frac{8.5999430 \times 10^9}{\lambda^2 - (215,0)^2} - \frac{9.1079005 \times 10^9}{\lambda^2 - (245,0)^2} + \frac{2.4117572 \times 10^9}{\lambda^2 - (287,0)^2} - \frac{1.6024598 \times 10^9}{\lambda^2}$$

d) in dioxane:

$$(\alpha)_\lambda^{20} = \frac{3.6987208 \times 10^9}{\lambda^2 - (215,0)^2} - \frac{5.0928960 \times 10^9}{\lambda^2 - (245,0)^2} + \frac{1.9569705 \times 10^9}{\lambda^2 - (287,0)^2} - \frac{2.6008704 \times 10^8}{\lambda^2}$$

e) in chloroform:

$$\begin{aligned}
 (M)_{\lambda}^{20} = & \frac{2.3932496 \times 10^9}{\lambda^2 - (215,0)^2} - \frac{3.5596889 \times 10^9}{\lambda^2 - (245,0)^2} + \frac{1.5744317 \times 10^9}{\lambda^2 - (287,0)^2} - \\
 & - \frac{1.0566437 \times 10^8}{\lambda^2}
 \end{aligned}$$

The values of molar rotations calculated by means of the above equations are given in brackets in Tab. 2. The agreement between the values calculated and those determined experimentally is fairly good.

Functions $(M)(\lambda)$ describing in the rectangular system of coordinates (λ is the independent variable) the optical properties of dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (10) change the sign, and have the extrema (two maxima and one minimum) within the range $0 < \lambda < \lambda_3$. Their asymptotes are the λ axis and the straight lines perpendicular to it at points 0, λ_1 , λ_2 and λ_3 .

In order to confirm the validity of the above equations $(M)(\lambda)$ we have determined in acetonitrile the circular dichroism (CD) and the UV spectrum of dextrorotatory enantiomer 10. The CD spectrum shows three strong positive maxima at $\lambda = 207$ nm ($(Q) = +37313,1$), $\lambda = 215$ nm ($(Q) = +37652,3$) and $\lambda = 287$ nm ($(Q) = +47489,4$) as well as one strong negative maximum at $\lambda = 245$ nm ($(Q) = -18995,8$). It is of interest that the CD spectra of optically active 2-(3'-bromobenzylsulfinyl)- and 2-(4'-bromobenzylsulfinyl)-benzoic acids are very similar. This fact confirms our hypothesis that the enantiomers rotating the plane of polarised light in same direction (in the visible part of the spectrum) have the same configuration.

The electronic spectrum shows in the examined region two strong absorption bands located in the region $\lambda = 210$ and 280 nm ($(\epsilon)_{210} = 37309,8$, $(\epsilon)_{280} = 3818,2$). A band which should appear in the region $\lambda = 245$ nm is probably screened by a nonsymmetric-from the long wave side-shape of the strong band located at $\lambda = 210$ nm.

It is significant that the wave lengths of the characteristic points on the circular dichroism curve (Q_{\max}) and the dispersion constants in the four-term equations determining the function $(M)(\lambda)$ have exactly the same values and that the signs of rotational constants are consistent with those of CD maxima. It should, however be mentioned that the positive CD maximum at $\lambda = 207$ nm is not represented in the four-term equations determining the functions $(M)(\lambda)$.

Analysis of the results of optical measurements leads to the conclusion that dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (10) shows in the examined spectral range three positive and one negative Cotton effects situated in the region $\lambda = 207, 215, 287$ and 245 nm.

The optical effects caused by introduction of bromine atom to the meta position of 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 the pronounced and diverse solvent effect. Dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid and its derivatives 11, 12 and 14 in all the solvents used in the measurement show molar rotations lower than those of the corresponding unsubstituted with bromine atom compounds. The relative average proc. decrease of molar rotations $\% \Delta R_{\text{mol}}$ for free acid is about $-1,84\%$; $-6,34\%$ for

its N-methylamide; - 3,28% for methyl ester and - 10,35% for p-nitrobenzyl ester. Introduction of bromine atom into the molecule of 2-(benzylsulfinyl)-benzoic acid in the meta position of the benzyl group decreases the rotation of the system in spite of its high molar rotation.

Unambiguous interpretation of the observed phenomena requires further systematic 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 dichrograph. The compounds were examined in suspensions in Nujal (IR) and in solutions mentioned in the text. ¹HNMR spectra were run on a Joel I NM-4H-100 (100 MHz) instrument in CDCl₃ as solvent using TMS as internal standard ($\delta = 0,00$ ppm). Elemental analyses were performed in our laboratory by A. Hoffman.

1. 2-(3'-Bromobenzylmercapto)-benzoic acid (1).

5 g of o-mercapto benzoic acid [8] dissolved in 250 ccm of water alkalinized with 5 g KOH was added in small portions with stirring to a solution of 5 g of bromobenzyl bromide [4,9] in 100 ccm of 96% ethanol. The mixture was stirred for 4 h maintaining the temperature in the reactor at 50-60°C. Then the solution was cooled and acidified to Congo with diluted (1:1 v/v HCl). A fine crystalline precipitate which soon separated was filtered off, washed with water, dried and crystallized from 96% ethanol (1 g subst./10 ccm solv.).

Colourless needles (7,5 g), m.p. 198-199°C. The product is readily soluble in chloroform, dioxane and acetone, sparingly soluble in methanol and 96% ethanol and insoluble in water.

Analysis:

For: $C_{14}H_{11}BrO_2S$ (323,2) - Calcd.: 52,0% C, 3,4 % H;

found: 52,2% C, 3,1 % H.

IR (cm^{-1}); 740, 990, 1220 δ $C_{Ar}-H$ (subst. 1, 2); 700, 800, 880, 1140 δ $C_{Ar}-H$ (subst. 1, 3); 1040 δ $C_{Ar}-H$ (subst. 1, 2 and 1,3); 1460, 1560, 1580 ν $C_{Ar}=C_{Ar}$; 1430 ν CH_2 ; 680 ν $C-S$; 1060 ν $C_{Ar}-Br$; 900 δ OH ; 1285, 1310, 1410 δ OH and ν $C-O$; 1670 ν $C=O(COOH)$.

2. Racemic 2-(3'-bromobenzylsulfinyl)-benzoic acid 2 .

10 g powdered acid 1 was suspended in 70 ccm of glacial acetic acid. The mixture was cooled to 0°C, was added 1,7 ccm 30% H_2O_2 and mechanically shaken at room temperature for 12 h. Then two portions of 1 ccm of 30% H_2O_2 were introduced to the suspension at 12 h intervals and it was shaken mechanically at room temperature for 24 h. A crystalline precipitate was filtered off, washed with water (30 ccm), dried in air and crystallized from 96% ethanol (1 g subst./ 10 ccm solv.). Colourless rods (7,5 g), m.p. 173°C with decomp.

The product is readily soluble in methanol, 96% ethanol and acetone, sparingly soluble in chloroform and dioxane and insoluble in benzene and water.

Analysis

For: $C_{14}H_{11}BrO_3S$ (339,2) - Calcd.: 49,6% C, 3,3% H;

found: 49,4% C, 3,4% H.

IR (cm^{-1}); 750, 1211 δ $C_{Ar}-H$ (subst. 1,2); 690, 800, 880, 1100,

1140 δ $C_{Ar}-H$ (subst. 1,3); 1050 δ $C_{Ar}-H$ (subst. 1,2 and 1,3);
 1470, 1570, 1590 ν $C_{Ar} = C_{Ar}$; 1438 ν CH_2 ; 680 ν $C-S$; 1070 ν
 $C_{Ar}-Br$; 1000 ν SO ; 900 δ OH ; 1280, 1300, 1410 δ OH and ν $C-O$;
 1700 ν $C=O$ ($COOH$).

3. Methyl ester of rac. 2-(3'-bromobenzylsulfinyl)-
 benzoic acid (3).

To a suspension of 4 g powdered acid 2 in 20 ccm of dry ether cooled externally with ice and water was introduced dropwise with stirring a solution of diazomethane in ether (prepared from 10 g of N,N' -nitrosomethylurea) until a permanent coloration appeared. Then the mixture was refluxed 1 h ($CaCl_2$ tube) on a water bath. The solvent was distilled off under reduced pressure (12 mm Hg, water bath). The solid residue (3 g) was crystallized from methanol (25 ccm). Colorless needles (2 g), m.p. $110^\circ C$. The ester is readily soluble in ether and acetone sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{15}H_{13}BrO_3S$ (353,2) - Calcd.: 51,0% C, 3,7% H;
 found: 51,3% C, 3,5% H.

4. Methyl amide of rac. 2-(3'-bromobenzylsulfinyl)-
 benzoic acid (4).

Powdered methyl ester (2 g) of rac. acid 2 was suspended in 30 ccm of 30% methylamine aq. solution and shaken mechanically for 10 h at room temperature. The reaction product was filtered off, washed with a water (30 ccm), dried in air and crystallized (1 g subst./5 ccm solv.) from methanol. Colorless needles (1,5 g), m.p. $191^\circ C$. The product is readily soluble in methanol, sparingly soluble in ether.

Analysis

For: $C_{15}H_{14}BrNO_2S$ (352,3) - Calcd.: 4,0% N;
found: 3,8% N.

5. p-Bromophenacyl ester of rac. 2-(3'-bromobenzyl-sulfinyl)-benzoic acid (5).

Rac. acid 2 (1,79 g, 5 mmole) and p-bromophenacyl bromide (1,39 g, 5 mmole) were used in esterification which was carried out for 3 h in 60 ccm of boiling 98% methanol. The product was filtered off (1,9 g) and crystallized from 96% ethanol (40 ccm). Colorless needles (1,3 g), m.p. 163°C. The ester is readily soluble in chloroform and acetone, sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{22}H_{16}Br_2O_4S$ (536,3) - Calcd.: 49,3% C, 3,0% H;
found : 49,0% C, 3,2% H.

6. p-Nitrobenzyl ester of rac. 2-(3'-bromobenzyl-sulfinyl)-benzoic acid (6).

Rac. acid 2 (1,7 g, 5 mmole) and p-nitrobenzyl bromide (1,1 g, 5 mmol) were used in esterification which was carried out for 3 h in 50 ccm of boiling 98% methanol. The product (1,5 g) was filtered off and crystallized from methanol (20 ccm). Colorless needles (1,1 g), m.p. 145°C. The ester is readily soluble in ethylene chloride, dioxane and acetone and sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{21}H_{16}BrNO_5S$ (474,3) - Calcd.: 2,9% N;
found : 2,8% N.

7. Brucine salt of laevorotatory 2-(3'-bromobenzyl-sulfinyl)-benzoic acid (7).

A sample of 5,088 g (0,015 mole) of acid 2 was mixed with 5,910 g (0,015 mole) of brucine and the mixture was dissolved in 90 ccm of 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. Needles (5 g), m.p. 118-123°C with decomp., $(\alpha)_D^{20} = -168,0^\circ$ ($c = 0,1$, $d = 0,5$, $\alpha = -0,084^\circ$) in 96% ethanol. After two crystallizations of the first fraction from 96% ethanol (I: 10.998 g, 90 ccm, 5 g, - 168°, 118-123°C; II: 5.0, 100, 3.0, - 178°, 120-121 ; III: 3.0, 90, 2.0, - 178°, 121) the product had physical properties which remained unchanged by further crystallization. Needles (2 g), m.p. 121°C, $(\alpha)_D^{20} = -178,0^\circ$ ($c = 0.1$, $d = 0.5$, $\alpha = -0.089^\circ$) in 96% ethanol. The salt is readily soluble in acetone and ethyl acetate, sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{37}H_{37}BrN_2O_7S$ (733,7) - Calcd.: 3,8% N;
found : 4,0% N.

8. Laevorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (8).

Brucine salt 7 (2 g, m.p. 121°C, $(\alpha)_D^{20} = -178,0^\circ$) was added to 50 ccm of warmed water. The mixture was stirred for several minutes and was carefully acidified to lacmus with 3% HCl. The resulting acid 8 was filtered off and was immediately dissolved in 50 ccm of 3% KOH. The solution was warmed to 50°C, filtered and acidified (lacmus) with 3% HCl.

The precipitate was filtered off (0,9 g), dried in air and crystallized from 25 ccm of 50% ethanol. Colorless plates (0,6 g), m.p. 192°C (decomp.), $(\alpha)_D^{20} = -355,0^\circ$ ($c = 0,1$, $d = 0,5$, $\alpha = -0,177^\circ$) in 96% ethanol. The product is readily soluble in methanol, 96% ethanol and acetone, sparingly soluble in dioxane and chloroform and insoluble in water.

Analysis

For: $C_{14}H_{11}BrO_3S$ (339,2) - Calcd.: 49,6% C, 3,3% H;

found: 49,9% C, 3,0% H.

IR (cm^{-1}): 750, 1210 $\delta C_{Ar}-H$ (subst. 1,2); 690, 800, 880, 1110, 1140 $\delta C_{Ar}-H$ (subst. 1,3); 1055 $\delta C_{Ar}-H$ (subst. 1,2 and 1,3); 1450, 1570, 1590 $\nu C_{Ar}=C_{Ar}$; 1430 νCH_2 ; 690 $\nu C-S$; 1070 $\nu C_{Ar}-Br$; 1010 νSO ; 900 δOH ; 1260, 1300, 1420 δOH and $\nu C=O$; 1690 $\nu C=O(COOH)$.

9. Brucine salt of dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (2).

The norther liquors from the first fraction of brucine salt of laevorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (section 7) were evaporated on a water bath to 40 ccm. The hot solution was filtered and allowed to stand at room temperature for 24 h. The resulting precipitate was filtered off. Colorless needles (4,5 g), m.p. 125-129°C (decomp.), $(\alpha)_D^{20} = +170,0^\circ$ ($c = 0,1$, $d = 0,5$, $\alpha = +0,085^\circ$) in 96% ethanol. After three crystallizations from 96% ethanol (I: 4.5 g, 50 ccm. 3.5 g, + 174,0°, 127-128°C; II: 3.5, 50, 3.0, + 178,0°, 128 III: 3.0, 50, 2.5, + 178.0, 128) the physical properties of the salt remained unchanged by further purification. Colorless needles (2,5 g) m.p. 128°C (decomp.), $(\alpha)_D^{20} = +178,0^\circ$ ($c = 0,1$, $d = 0,5$, $\alpha = +0,089^\circ$) in 96% ethanol. The salt is readily soluble in

acetone and ethyl acetate, sparingly soluble in methanol, 96% ethanol and dioxane and insoluble in water.

Analysis

For: $C_{37}H_{37}BrN_2O_7S$ (733,7) - Calcd.: 3,8% N;

found : 3,9% N.

10. Dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (10).

Brucine salt 9 (2,5 g, m.p. 128°C, $(\alpha)_D^{20} = +178,0^\circ$) was converted into free acid as in section 8. Crude acid (1,2 g) was crystallized from 50% ethanol (30 ccm). Colorless needles (0,7 g), m.p. 197°C (decomp.), $(\alpha)_D^{20} = +360,0^\circ$ (c = 0,1, d = 0,5, $\alpha = +0,180^\circ$ in 96% ethanol. The acid is readily soluble in methanol, 96% ethanol and acetone, sparingly soluble in chloroform and dioxane and insoluble in water.

Analysis

For: $C_{14}H_{11}BrO_3S$ (339,2) - Calcd.: 49,6% C, 3,3% H;

found : 49,9% C, 3,3% H.

11. Methyl ester of dextrorotatory 2-(3'-bromobenzylsulfinyl)-benzoic acid (11).

Acid 10 (2 g) was converted into methyl ester as in section 3. The transformation product (1,8 g) was crystallized from methanol (20 ccm). Colorless needles (1 g), m.p. 102°C, $(\alpha)_D^{20} = +338,0^\circ$ (c = 0,1, d = 0,5, $\alpha = +0,169^\circ$) in 96% ethanol. The ester is readily soluble in ether and acetone and sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{15}H_{13}BrO_3S$ (353,2) - Calcd.: 51,0% C, 3,7% H;

found : 51,1% C, 3,5% H.

12. Methylamide of dextrorotatory 2-(3'-bromobenzylsulfanyl)-benzoic acid (12).

Methyl ester 11 (2 g) was converted into the corresponding methylamide as in section 4. The product was crystallized from methanol (1 g subst./ 5 ccm solv.). Colorless needles (1,5 g), m.p. 174-175°C, $(\alpha)_D^{20} = + 292,0^\circ$ (c = 0,1, d = 0,5, $\alpha = + 0,146^\circ$) in 96% ethanol. The product is readily soluble in methanol and 96% ethanol and sparingly soluble in ether.

Analysis

For: $C_{15}H_{14}BrNO_2S$ (352,2) - Calcd.: 4,0% N;
found : 4,1% N.

13. p-Bromophenacyl ester of dextrorotatory 2-(3'-bromobenzylsulfanyl)-benzoic acid (13).

1,79 g of dextrorotatory acid 10 and 1,39 g of p-bromophenacyl bromide were converted into the corresponding p-bromophenacyl ester as in section 5. The transformation product (1,7 g) was crystallized from 96% ethanol (40 ccm). Colorless needles (1,1 g), m.p. 179-180°C, $(\alpha)_D^{20} = + 274,0^\circ$ (c = 0,1, d = 0,5, $\alpha = + 0,137^\circ$) in 96% ethanol. The product is readily soluble in acetone and chloroform and sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{22}H_{16}Br_2O_4S$ (536,2) - Calcd.: 49,3% C, 3,0% H;
found : 49,4% C, 2,9% H.

14. p-Nitrobenzyl ester of dextrorotatory 2-(3'-bromo-benzylsulfinyl)-benzoic acid (14).

1,7 g of dextrorotatory acid 10 and 1,1 g of p-nitrobenzyl bromide were converted into the corresponding p-nitrobenzyl ester as in section 6. The product was filtered off (1,4 g) and crystallized from 96% ethanol (20 ccm). Colorless needles (1,1 g), m.p. 161°C, $(\alpha)_D^{20} = +284,0^\circ$ ($c = 0,1$, $d = 0,5$, $\alpha = +0,142^\circ$) in 96% ethanol. The ester is readily soluble in dioxane and acetone and sparingly soluble in methanol and 96% ethanol.

Analysis

For: $C_{21}H_{16}BrNO_5S$ (474,3) - Calcd.: 2,9% N;
found : 3,0% N.

15. 2-(3'-Bromobenzylsulfonyl)-benzoic acid (15).

A suspension of 10 g of acid 1 in 50 ccm of glacial acetic acid was treated with 8 ccm of 30% H_2O_2 and was refluxed for 20 h. The hot solution was allowed to crystallize at room temperature. A fine crystalline precipitate separated. It was filtered off (6 g) and crystallized from 96% ethanol (45 ccm). Colorless needles (4,5 g), m.p. 177-179°C. This sulfone is readily soluble in acetone and ethyl acetate, sparingly soluble in methanol, 96% ethanol and glacial acetic acid and insoluble in water.

Analysis

For: $C_{14}H_{11}BrO_4S$ (355,2) - Calcd.: 47,4% C, 3,1% H;
found : 47,6% C, 3,0% H.

IR (cm^{-1}); 760, 1000 $\delta C_{Ar}-H$ (subst. 1,2); 690, 795, 860, 1130 $\delta C_{Ar}-H$ (subst. 1,3); 1080 $\delta C_{Ar}-H$ (subst. 1,2 and 1,3);

1440, 1570, 1580 $\nu_{\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}}$; 1430 ν_{CH_2} ; 680 $\nu_{\text{C-S}}$; 720 $\nu_{\text{C}_{\text{Ar}}-\text{Br}}$; 1150 ν_{sSO_2} ; 1310 ν_{asSO_2} ; 900 δ_{OH} ; 1270, 1410 δ_{OH} and $\nu_{\text{C-O}}$; 1690 $\nu_{\text{C=O(COOH)}}$.

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

Rac. acid 2 (1 g) was suspended in 30 ccm of acetic anhydride and heated (bath temperature 100°C) for 2 h. The solution was cooled to 10°C and neutralized to lacmus with 10% Na_2CO_3 . The product was extracted with benzene (3 x 30 ccm). The extracts were combined and were washed with water and dried with anhydrous MgSO_4 . The solvent was distilled off under reduced pressure (12 mm Hg, water bath). The residue was crystallized from 96% ethanol (1 g subst./5 ccm solv.). Colorless needles (0,6 g), m.p. 121°C. Yield 63%. The product is readily soluble in chloroform, methanol and benzene, sparingly soluble in dioxane and acetone and insoluble in water.

Analysis

For: $\text{C}_{14}\text{H}_9\text{BrO}_2\text{S}$ (321,2) - Calcd.: 52,3% C, 2,8% H;

found: 52,3% C, 2,7% H.

IR (cm^{-1}); 740, 1000, 1215 $\delta_{\text{C}_{\text{Ar}}-\text{H}}$ (subst. 1,2); 700, 780, 880, 1100, 1160 $\delta_{\text{C}_{\text{Ar}}-\text{H}}$ (subst. 1,3); 1030, 1045 $\delta_{\text{C}_{\text{Ar}}-\text{H}}$ (subst. 1,2 and 1,3); 1460, 1570, 1580 $\nu_{\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}}$; 1440 ν_{CH} ; 680 $\nu_{\text{C-S}}$; 700 $\nu_{\text{C}_{\text{Ar}}-\text{Br}}$; 1250, 1280 $\nu_{\text{C-O}}$; 1710 $\nu_{\text{C=O}}$.

17. Dextrorotatory 3-(3'-bromophenyl)-4-thiaisochroman-1-one (17).

Dextrorotatory acid 10 (1 g) was converted into dextrorotatory 3-(3'-bromophenyl)-4-thiaisochroman-1-one as in section 16. The crude product was crystallized from 96% ethanol (1 g subst./5 ccm solv.). Colorless needles (0,55 g), m.p.

121°C , $(\alpha)_{\text{D}}^{20} = + 6,5^{\circ}$ ($c = 0,1$, $d = 0,5$, $\alpha = + 0,0035^{\circ}$) in 96% ethanol. Yield 58%. The product is readily soluble in chloroform, benzene, methanol and 96% ethanol, sparingly soluble in dioxane and acetone and insoluble in water.

Analysis

For: $\text{C}_{14}\text{H}_9\text{BrO}_2\text{S}$ (321,2) - Calcd.: 52,3% C, 2,8% H;

found : 52,2% C, 2,7% H.

IR (cm^{-1}): 760, 1000, 1220 δ $\text{C}_{\text{Ar}}-\text{H}$ (subst. 1,2); 700, 780, 880, 1100, 1160 δ $\text{C}_{\text{Ar}}-\text{H}$ (subst. 1,3); 1030, 1045 δ $\text{C}_{\text{Ar}}-\text{H}$ (subst. 1,2 and 1,3); 1440 \vee CH; 680 \vee C-S; 740 \vee $\text{C}_{\text{Ar}}-\text{Br}$; 1250, 1280 \vee C-O; 1710 \vee C=O.

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S T R E S Z C Z E N I E

Opisano syntezę i podstawowe własności kwasów 2-(3'-bromobenzylsulfinylo)- i 2-(3'-bromobenzylsulfonylo)-benzoesowych. Racemiczny sulfotlenek rozszczepiono w drodze krystalizacji frakcyjnej jego soli z brucyną na enancjomery optyczne. Na podstawie przeprowadzonych badań korelacyjnych przypisano poszczególnym enancjomerom bezwzględne konfiguracje. Zdefiniowano w rejonie $360 < \lambda < 623,4$ nm dyspersję optycznej rotacji lewoskrętnego enancjomeru oraz jego pochodnej metyloamidowej i pochodnych estrowych. Wyznaczono czterocząłkowe równania opisujące rotację optyczną prawoskrętnego kwasu w badanym za-

kresie widmowym. Określono metodami kinetyki klasycznej stałe racemizacji (K) oraz parametry aktywacji (E_a , ΔS^\ddagger , ΔH^\ddagger) dla procesu racemizacji prawoskrętnego kwasu 2-(3'-bromobenzylsulfinylo)-benzoesowego. Wykonano przegrupowanie prawoskrętnego kwasu 2-(3'-bromobenzylsulfinylo)-benzoesowego do prawoskrętnego - 3-(3'-bromofenylo)-izo-4-tia-chroman-1-onu.

РЕЗЮМЕ

Описано синтез и основные свойства кислот 2-/3'-бромбензилсульфинил/ и 2-/3'-бромбензилсульфонил/-бензойных. Рацемическую сульфокислоту расщеплено в ходе фракционной кристаллизации ее соли с бруциной на оптические зеркальные изомеры. На основе проведенных корреляционных исследований приписано отдельным зеркальным изомерам относительные конфигурации. Определено в районе $360 < \lambda < 623,4$ нм дисперсию оптического вращения левовращающего зеркального изомера, его метиламидовой производной и производных сложных эфиров. Выделено четырехчленное уравнение, описывающее оптическое вращение правовращающей кислоты в исследованном диапазоне спектра. Определено методами классической кинетики постоянные рацемизации K и параметры активации $E_a, \Delta S^\ddagger, \Delta H^\ddagger$ для процесса рацемизации правовращающей кислоты 2-/3'-бромбензилсульфинил/-бензойной. Выполнено перегруппование правовращающей кислоты 2-/3'-бромбензилсульфинил/-бензойной в правовращающий 3-/3'-бромфенил/-изо-4-тио-хроманон.

