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Effect of Molecular Structure on Optical Properties of Systems Containing Carbon Chirality Centers. XX.* Synthesis, Spatial Configuration and Optical Properties of α-(1,5-Bromonaphthyl)-Propionic Acids**

Wpływ budowy cząsteczkowej na własności optyczne układów z węglowymi centrami chiralności. XX. O syntezie, konfiguracji przestrzennej i własnościach optycznych. kwasów α-(1,5-bromonaftylo)-propionowych

Влияние молекулярного строения на оптические свойства расположений с угольными центрами хиральности. XIX. ... О синтезе пространственной конфигурации и оптических особенностях α-(1,5-бромонафтило)-припионовых кислот

The problem of the effect of position isomerism of halogen atom in the aromatic ring on optical properties of aromatic-aliphatic compounds containing carbon chirality centers is studied in our laboratory on the example of bromo derivatives of α-(1- and 2-naphthyl)-propionic acids. In the previous communications we described the synthesis and the principal chiralooptical properties of enantiomeric α-(1-naphthyl)--propionic acids and their 4- and 7-bromo derivatives [1, 2, 3]. In these studies we found that:

1) the enantiomers rotating the plane of polarized light in the same direction have the same spatial configurations;

2) the optically active acids have normal rotatory dispersion in the visible part of the spectrum;

3) as a rule, 1,4-bromonaphthylpropionic acids have lower, and 7,1-bromonaphthyl-

* Part XIX, Janczewski M., Jabłońska-Pikus T.: Pol. J. Chem., in press. Preliminary communication – Janczewski M., Jabłońska-Pikus T.: Pol. J. Chem., 52, 663 (1978).

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propionic acids higher molar rotations than those of unsubstituted systems of the same spatial structure.

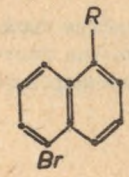
The observed optical and stereochemical rules encouraged us to more extensive studies. In the present communication we are reporting the results of studies on synthesis and principal optical and stereochemical properties of enantiomeric α-(1,5-bromonaphthyl)-propionic acids.

The starting material in the synthesis of the principal system, i.e. acid 1, was 1-naphthaldehyde, which after bromination in position 5 in chloroform [4] was reduced with lithium aluminium hydride in ether to 1,5-bromohydroxymethylnaphthalene [5]. This carbinol under the influence of phosphorus tribromide in carbon tetrachloride gave a good yield of 1,5-bromo-bromomethyl-naphthalene [5] which was readily converted into bromo-cyanomethyl-naphthalene under the conditions described in the literature [6]. The nitrile was hydrolized to free 1,5-bromonaphthylacetic acid (1) by means of potassium hydroxide in dilute ethanol [6]. The structure of acid 1 was unambiguously confirmed by:

a) elemental analysis,

b) synthesis of its amide (2) and methyl, p-nitrobenzyl and p-bromophenacyl- esters (3, 4 and 5 respectively);

c) analysis of its ir spectrum and of ir spectrum of its amide (2) (characteristic bands are given in the experimental part).



1: $R=CH_2\cdot COOH$
2: $R=CH_2\cdot CO\cdot NH_2$
3: $R=CH_2\cdot CO\cdot OCH_3$
4: $R=CH_2\cdot CO\cdot OCH_2\cdot C_6H_4\cdot NO_2$
5: $R=CH_2\cdot CO\cdot OCH_2\cdot CO\cdot C_6H_4Br$
6: $R=CH(CH_3)\cdot COOH$ (±)
7: $R=CH(CH_3)\cdot CO\cdot NH_2$ (±)
8: $R=CH(CH_3)\cdot CO\cdot OCH_2\cdot C_6H_4\cdot NO_2$ (±)
9: $R=CH(CH_3)\cdot CO\cdot OCH_2\cdot CO\cdot C_6H_4Br$ (±)
10: $R=CH(CH_3)\cdot COOH\cdot$ Bruc.* (+)
11: $R=CH(CH_3)\cdot COOH$ (+)
12: $R=CH(CH_3)\cdot COOH\cdot$ Cinchd.** (–)
13: $R=CH(CH_3)\cdot COOH$ (–)
14: $R=CH(CH_3)\cdot CO\cdot NH_2$ (+)
15: $R=CH(CH_3)\cdot CO\cdot OCH_2\cdot C_6H_4\cdot NO_2$ (+)

* Bruc. – brucine.
** Cinchd. – cinchonidine.

Racemic α-(1,5-bromonaphthyl)-propionic acid (6) which is a new compound, was prepared in a fairly good yield by methylation of acid 1 with methyl iodide in the presence of sodium derivative of naphthalene in anhydrous diethyl ether. The structure of compound 6 was fully confirmed by elemental analysis and ir spectrum (characteristic bands are given in the experimmental part). Is should be mentioned that acid 6 froms readily crystallizing amide (7) and p-nitrobenzyl- and p-bromophenacyl esters (8 and 9).

In our further studies we attempted the resolution of acid 6 by crystallization of its diastereomeric salts with alkaloids. We obtained the best results using brucine and cinchonidine. The salts with other alkaloids could be readily prepared and crystallized well, but were unsuitable for a rapid separation of the antimers. The brucine was very suitable for this purpose since its salt with the dextrorotatory enantiomer was less soluble in acetone than that with the laevorotatory antipode. After three crystallizations we obtained optically pure salt of the dextrorotatory acid 10 (m. p. 144–145°, $[\alpha]_D^{20}$ = = −20.0° in acetone). The cinchonidine salt with the racemic acid 6 on crystallization from acetone contained the laevorotatory enantiomer in the front fractions. After four crystallizations we obtained optically homogeneous salt 12 (m. p. 141–143°, $[\alpha]_D^{20}$ = = −80.5° in acetone) of the laevorotatory antimer.

Optically active α-(1,5-bromonaphthyl)-propionic acids (11 and 13) liberated in the usual way from the alkaloids had, after crystallization from benzene and petroleum ether, relatively low specific rotations ($[\alpha]_D^{20} = \pm 53.0°$).

Comparison of melting points and solubilities of enantiomers 11 and 13 with those of racemic acid 6 indicates that the latter is a true racemate.

Infrared spectra measured in paraffin oil confirm our observations. They are identical for both optical antimers but differ considerably from the spectrum of racemic acid 6 which has apparently a different crystallochemical structure in the solid state. The most pronounced differences occur in the carbonyl stretching vibrations band. In the case of racemate 6 there is one sharp band at 1696 cm^{-1} and in the spectrum of the enantiomers – a doublet at 1680 and 1718 cm^{-1}. A similar splitting of the stretching vibrations band in stereoisomeric systems was observed by us in the case of α-(1,4)- and α-(1,7)- bromonaphthylpropionic acids [2, 3].

In order to obtain sufficient material for optical studies we have prepared amide 14 and p-nitrobenzyl ester 15 of dextrorotatory acid 11. We carried out model experiments on optically inactive substrates. It can be assumed that the mild conditions of the syntheses did not cause racemization at the carbon chirality centre. We measured the molar rotations of dextrorotatory acid 11 and of its derivatives 14 and 15 in Perkin-Elmer spectropolarimeter 241-MC in methanol (M), ethanol (E), acetone (A), dioxane-(D) and chloroform (Ch) at λ = 600, 589, 560, 520, 480, 440, 400, 380, 360, 330, 320, 310 and 300 nm.

The results of these measurements show that the molar rotations largely depend on the character of the solvent.

The solvent series arranged according to decreasing values of molar rotation for free acid (11, I), its amide (14, II) and p-nitrobenzyl ester (15, III) are as follows: I: A > D > > Ch > E > M; II: D > A > E > M > Ch; III: D > Ch > E > M > A. These series are considerably different but they are similar to those of dextrorotatory α-(7,1-bromo--naphthyl)-propionic acid and its derivatives having analogous structures [3]. It should be stressed that the decreases of molar rotations caused by the changes of solvents in the order shown in the series are in general moderate with the exception of a considerable decrease in the case of the acid amide in chloroform methanol and ethanol solutions. The dependence of the molar rotation of the wave length in the visible part of the spectrum can be approximately described by one-term Drude equations, which indicates that the optical rotatory dispersion of the examined compounds in this region is normal. It is

Table 1. Optical rotatory dispersion of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid and some of its derivatives

Compound	Solvent	Molar rotation $[M]_\lambda^{20}$										
		λ=600 nm	λ=589 nm	λ=560 nm	λ=520 nm	λ=480 nm	λ=440 nm	λ=400 nm	λ=380 nm	λ=360 nm	λ=340 nm	λ=320 nm
Dextrorotatory α-(1,5-bromonaphthyl)-propionic acid	A	187.0	193.9	223.3	267.9	334.9	435.4	588.9	692.2	848.5	1083.0	580.5
		(185.5)	(194.2)	(220.6)	(267.6)	(333.4)	(430.5)	(585.7)	(702.0)	(861.2)	(1073.4)	(582.3)
	Ch	150.7	157.7	178.6	217.7	273.5	351.7	482.9	572.2	703.4	887.6	530.3
		(151.3)	(158.4)	(179.9)	(218.3)	(271.9)	(351.5)	(478.8)	(574.5)	(706.4)	(886.2)	(530.5)
	D	170.3	177.2	203.8	242.8	304.2	396.4	530.3	625.2	764.8	960.2	569.4
		(169.0)	(176.9)	(200.8)	(243.5)	(303.1)	(390.8)	(530.1)	(633.7)	(773.5)	(952.6)	(571.0)
	E	142.4	147.9	170.3	206.6	262.4	343.3	466.1	547.1	664.3	826.2	513.6
	M	139.6	146.5	167.5	200.9	251.2	323.8	446.6	524.8	642.0	792.7	505.4
		(140.3)	(146.9)	(166.8)	(202.3)	(251.8)	(324.8)	(440.7)	(527.0)	(643.5)	(792.3)	(502.4)
Dextrorotatory α-(1,5-bromonaphthyl)-propionic acid amide	A	116.8	122.4	139.0	169.7	205.8	272.6	367.2	428.3	511.8	559.2	358.8
	Ch	63.9	68,1	77.9	94.6	116.8	155.7	216.9	264.2	350.5	467.3	261.5
	D	125.2	129.3	147.4	178.0	222.5	294.8	394.9	478.4	584.1	745.4	406.1
	E	75.1	79.3	89.0	108.5	133.5	175.2	233.6	272.6	342.1	428.3	244.8
	M	66.8	70.9	80.6	97.3	122.4	158.5	222.5	255.9	322.6	400.5	230.9
p-nitrobenzyl ester of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid	A	281.6	294.1	339.7	414.2	513.7	687.6	961.1	1177.5	1449.9	1512.0	745.6
	Ch[1]	302.4	318.9	364.6	439.1	563.4	737.3	1027.3	1284.2	1599.0	2154.1	845.1
	D	314.8	327.3	372.8	463.9	579.9	770.5	1072.9	1313.2	1640.4	2133.4	861.6
	E	289.9	302.4	347.9	422.5	530.2	704.2	985.5	1217.9	1565.8	1988.4	836.8
	M	285.8	298.3	343.8	418.4	521.9	695.9	973.5	1188.9	1512.0	2313.2	795.4

c = 0.1 g/100 ccm.

A – acetone, Ch – chloroform, D – dioxane, E – ethanol, M – methanol.

significant that the differences between the molar rotations of the free acid 11, its amide 14 and its p-nitrobenzyl ester 15 are fairly large in all the solvents in the whole visible part of the spectrum. The rotation relationships make it possible to determine the spatial configurations of optically active acids 11 and 13, on the basis of Freudenberg shift rule, and the direction of changes of molar rotation, caused by suitable choice of solvents, for the reference systems and for the examined compounds. For both cases we were using the unsubstitued system, i.e. dextrorotatory α-(1-naphthyl)-propionic acid as the configurational standard. The spatial structure of enantiomeric α-(1-naphthyl)-propionic acids was unambiguously determined by Fredga [7] who ascribed the absolute configuration S(+) to the dextrorotatory enantiomer and R(−) to its antipode. The Freudenberg directions of rotation shifts, determined in sodium light in methanol, ethanol, acetone, chloroform and dioxane for the standard and for compound 11 on passing from p-nitrobenzyl esters to free acids and their amides are in good agreement. This proves unambiguously that the enantiomers rotating the plane of polarized light in the same direction have the same configurations and that the dextrorotatory acid 11 has the absolute configuration S(+). This conclusion is confirmed by the changes in molar rotation of dextrorotatory

Table 2. Molar rotations $(M)_D^{20}$ of dextrorotatory α-(1-naphthyl)-propionic and α-(1,5-bromonaphthyl)-propionic acids and of some of their derivatives

		Compound	
		α-(1-naphthyl)--propionic acid	α-(1,5-bromonaphthyl)--propionic acid
Acetone	p-Nitro-benzyl ester	325.3	294.1
	Acid	292.3	193.9
	Amide	175.3	122.4
Chloroform	p-Nitro-benzyl ester	345.4	318.9
	Acid	254.3	157.7
	Amide	87.7	68.1
Dioxane	p-Nitro-benzyl ester	331.9	327.3
	Acid	266.3	177.2
	Amide	166.4	129.3
Ethanol	p-Nitro-benzyl ester	335.5	302.4
	Acid	238.3	147.9
	Amide	118.3	79.3
Methanol	p-Nitro-benzyl ester	348.7	298.3
	Acid	234.3	146.5
	Amide	115.6	70.9

Table 3. Effect of solvents on the rotation of dextrorotatory α-(1-naphthyl)-propionic (I) and α-(1,5-bromonaphthyl)-propionic (II) acids

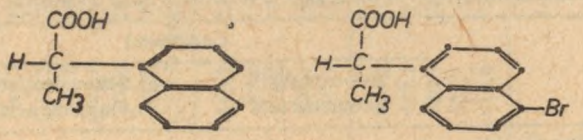
Solvent	$[M]_D^{20}$	
	Acid I	Acid II
Acetone	292.3	193.9
Dioxane	266.3	177.2
Chloroform	254.3	157.7
Ethanol	238.3	147.9
Methanol	234.3	146.5

Table 4. Effect of solvents on the rotation of dextrorotatory amides of α-(1-naphthyl)-propionic (I) and α-(1,5-bromonaphthyl)-propionic (II) acids

Solvent	$[M]_D^{20}$	
	Amide of acid I	Amide of acid II
Acetone	175.3	122.4
Ethanol	118.5	79.2
Methanol	115.6	70.9
Chloroform	87.7	68.1

α-(1-naphthyl)-propionic and α-(1,5-bromonaphthyl)-propionic acid 11 as well as their amides, caused by the solvents, shown in tables 3 and 4.

The agreement between the directions of the directions of the rotational changes indicates that the stereochemical structures of the examined systems are indentical. The spatial relationships can be represented by the following projection formulae:



S(+) S(+)

On the basis of the data collected in Table 1 ($320\ nm < \lambda < 600\ nm$) we determined functions $[M](\lambda)$ for dextrorotatory α-(1,5-bromonaphthyl)-propionic acid in four solvents. These functions have the character of three-term equations* which we give below:

a) in methanol:

$$[M]_\lambda^{20} = \frac{-265 \times 10^4}{\lambda^2 - (315.0)^2} + \frac{437 \times 10^5}{\lambda^2 - (264.3)^2} + \frac{123}{\lambda^2 - (226.8)^2}$$

b) in acetone:

$$[M]_\lambda^{20} = \frac{-241 \times 10^4}{\lambda^2 - (316.7)^2} + \frac{565 \times 10^5}{\lambda^2 - (263.9)^2} + \frac{124 \times 10^3}{\lambda^2 - (227.3)^2}$$

* The equations were determined by the least squares method and the conjugated gradient algorithm for finding the functions of many variables (mathematical machine ODRA-1013).

c) in chloroform:

$$[M]_{\lambda}^{20} = \frac{-165 \times 10^4}{\lambda^2 - (317.0)^2} + \frac{458 \times 10^5}{\lambda^2 - (263.8)^2} + \frac{101 \times 10^2}{\lambda^2 - (227.3)^2}$$

d) in dioxane:

$$[M]_{\lambda}^{20} = \frac{-297 \times 10^4}{\lambda^2 - (315.4)^2} + \frac{523 \times 10^5}{\lambda^2 - (263.7)^2} + \frac{118 \times 10^3}{\lambda^2 - (226.8)^2}$$

The values of molar rotation calculated on the basis of the above equations are shown in brackets in Table 1. The agreement between the calculated and the experimmental values is good.

Functions $[M](\lambda)$ describing the optical properties of dextrorotatory α-(5-bromo-1-naphthyl)-propionic acid in the rectangular systems of coordinates (λ is the independent variable) change the sign and have the exterma as well as the inflexion points in the range $\lambda_3 < \lambda < \lambda_1$. Their asymptotes are the λ axis and the straight lines perpendicular to it at λ_1, λ_2 and λ_3.

The circular dichroism curves determined in acetonitrile for the dextrorotatory enantiomer 11 have two positive maxima at λ = 230 nm ([Θ] = 67158.2) and λ = 272 nm ([Θ] = 9858.1), one very weak positive maximum at λ = 323 nm, one inflexion at λ = = 315 nm and one negative maximum at 220 nm ([Θ] = −22796.6). This should be compared with the circular dichroism curves determined in dioxane for dextrorotatory (S+) α-(1-naphthyl)-propionic acid, which show only one strong maximum at λ = 234 nm ([Θ] = 12199.6), one very weak maximum at λ = 318 nm ([Θ] = 108.4) and in contrast to acid 11 one strong negative maximum at λ = 283 nm ([Θ] = −3727.7). The extrema of the CD curves of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid indicate that the examined system 11 exhibits three positive and one negative Cotton effect. These effects, with the exception of extreme long wave (λ = 323 nm) and short wave (λ = 220 nm) are situated in the regions determined by the dispersion constans of the three-term equations of functions $[M](\lambda)$. It should be observed that the sign of the long wave Cotton effect changes on passing from the unsubstituted system (dextrorotatory α-(1-naphthyl)-propionic acid; λ = 283 nm) to the system substituted with bromine atom in position ana (dextrorotatory α-(1,5-bromonaphthyl)-propionic acid, λ = 272 nm). A similar relationship was observed by Korver [9] in the group of halogen derivatives of mandelic acid. The isomers containing halogen atom in benzene ring in positions ortho and para had the sign of the long wave Cotton effect (^1L_b, $250 < \lambda < 275$) opposite to that of the unsubstituted system and its meta haloderivatives. In our previous publications [8, 10, 11] we have pointed out the optical difference between the unsubstituted systems and their ortho and para haho- and methoxy derivatives in the group of naphthalene derivatives containing carbon or heteroatomic chirality centers, and we have proposed our own interpretation of our observations, having the character of a working hypothesis.

The UV spectrum of acid 11 (in 96% ethanol) has two groups of bands. The band in the region $220 < \lambda < 250$ nm has a strong maximum at λ = 230 nm (ϵ = 47423.3; probl. trans. $\Pi \rightarrow \Pi^*$ (^1B_b)) and a distinct inflexion at 214 nm (ϵ = 23851.4; probl. trans.

$n \rightarrow \Pi^*(COOH)$). The second group in the region $260 < \lambda < 310$ nm has three strong maxima at $\lambda = 284$ nm ($\epsilon = 6401.3$), $\lambda = 292$ nm ($\epsilon = 7932.4$; probl. trans. $\Pi \rightarrow \Pi^* {}^1L_a$ and $\lambda = 304$ nm ($\epsilon = 5799.7$) as well as an inflexion at $\lambda = 272$ nm ($\epsilon = 3171.2$). At the extreme long wave region there is another, very weak band at $\lambda = 318$ nm ($\epsilon = 877.4$; probl. trans. $\Pi \rightarrow \Pi^* {}^1L_b$). Dextrorotatory α-(1-naphthyl)-propionic acid (in 96% ethanol) has analogical spectrum. In the region $200 < \lambda < 250$ nm there is a strong maximum at $\lambda = 226$ nm ($\epsilon = 40046.4$; probl. trans. $\Pi \rightarrow \Pi^* {}^1B_b$) and a distinct inflexion at $\lambda = 210$ nm ($\epsilon = 25221.0$; probl. trans. $n \rightarrow \Pi^*(COOH)$). In the region $260 < \lambda < 310$ nm there are strong maxima at $\lambda = 274$ nm ($\epsilon = 6307.0$), $\lambda = 284$ nm ($\epsilon = 7573.2$; probl. trans. $\Pi \rightarrow \Pi^* {}^1L_a$ and $\lambda = 294$ nm ($\epsilon = 5359.0$) as well as one inflexion at $\lambda = 264$ nm ($\epsilon = 3350.3$). In the extreme long wave region there is another, very weak band at 316 nm ($\epsilon = 539.4$ probl. trans. $\Pi \rightarrow \Pi^* {}^1L_b$). The wave lenghts of the optically active bands at $\lambda = 230$, 272 and 318 nm in the UV spectrum of acid 11 are in a fairly good agreement with the values of dispersion constans of the three-term equations quoted above. The term containing the dispersion constans corresponding to the passage in the region $\lambda = 214$ nm ($\lambda_{\theta max} = 220$ nm) is absent in the equations of $[M](\lambda)$, which is probably due to the weak rotation corresponding to this term and to the insufficient sensitivity of the apparatus used in our studies. For the same reasons the term corresponding to the positive maximum of the CD curve in the region $\lambda = 323$ nm was absent from the equations of $[M](\lambda)$.

The optical effect caused by the introduction of bromine atom to the arene nucleus of the molecule of α-(1-naphthyl)-propionic acid in the region of λ values, for which the optical rotatory dispersion is normal, are sometimes difficult to determine unambiguosly due to different and considerable effect of the solvents used in the measurements. The clearest effect are obtained for free acid 11, its amide 14 and p-nitobenzyl ester 15. In all the solvents used in the measurements, these compounds had molar rotations much lower than the corresponding unsubstituted systems containing no halogen atoms in the naphthalene rings. Table 5 clearly shows the optical relationships in the group of the examined bromo derivatives of α-(1-naphthyl)-propionic acid containing the substituents in the quinonoidal positions (isomers 1,4; 1,5 and 1,7).

Comparison of the collected numerical data shows that the introduction of bromine atom to position kata of the molecule of α-(1-naphthyl)-propionic acid, its amide or its p-nitrobenzyl ester, causes a strong increase of the molar rotation irrespective of the character of the solvent, whereas the introduction of bromine atom to position ana causes a strong decrease of the molar rotation, already emphasized by us. The effect of substitution in the para position is much weaker. The observed relationships are very similar to the changes in molar rotation connected with the position isomerism of bromine atom in the naphthalene nucleus in the group of 1-naphthylsulfinylacetic acid derivatives [θ]. It is difficult to reach an unambiguous interpretation of all these observations, however it is possible to explain the optical relationships observed in the present study, as in the case of previously examined compounds [8], by the changes in the charge density in the vicinity of the carbon chirality center, caused by the influence of the opposing effects, i.e. the mesomeric effect (+M) and the inductive effect (–I) of the halogen atom on the free electrons of the aromatic nucleus.

Table 5. Effect of substituents on molar rotation of dextrorotatory α-(1-naphthyl)-propionic acid and some of its derivatives

No.	Substituent	Position of substituent in naphthalene nucleus	Solvent	Acid		Amide		p-Nitrobenzyl ester	
				$[M_n]_D^{20}$	%ΔM.r.	$[M_n]_D^{20}$	%ΔM.r.	$[M_n]_D^{20}$	%ΔM.r.
1	–	–	Acetone	292.3	–	175.30	–	325.3	–
			Chloroform	254.3	–	87.70	–	345.4	–
			Dioxane	266.3	–	166.40	–	332.0	–
			Ethanol	238.3	–	118.50	–	355.5	–
			Methanol	234.3	–	115.60	–	348.7	–
2	Br	4	Acetone	273.5	−6,43	208.60	+18.98	260.9	−19.77
			Chloroform	228.9	−9.99	119.60	+36.42	277.5	−19.64
			Dioxane	238.7	−10.38	219.70	+32.12	265.1	−20.14
			Ethanol	220.5	−7.45	136.29	+14.96	302.4	−14.93
			Methanol	206.5	−11.83	125.20	+8.32	285.8	−18.04
3	Br	5	Acetone	194.0	−33.64	122.40	−30.19	294.1	−9.58
			Chloroform	157.7	−37.98	68.10	−22.26	318.9	−7.65
			Dioxane	177.2	−33.44	129.30	−22.22	327.3	−1.42
			Ethanol	147.9	−37.90	79.30	−33.13	302.4	−14.93
			Methanol	146.5	−37.40	70.90	−38.62	298.3	−14.48
4	Br	7	Acetone	401.9	+37.49	300.40	+71.30	532.3	+63.65
			Chloroform	350.3	+37.76	189.10	+115.74	577.9	+67.31
			Dioxane	365.7	+37.30	325.40	+95.63	575.8	+73.44
			Ethanol	354.5	+48.77	242.00	+104.12	546.8	+53.83
			Methanol	339.1	+44.76	242.00	+109.41	538.5	+54.41

$n = 1, 2, 3, 4.$

$$\%\Delta M.r. = \frac{[M_n]_D^{20} - [M_1]_D^{20}}{[M_1]_D^{20}} \cdot 100$$

Our studies on the optical relationships in the group of isomeric α-(bromo-2-naphthyl)-propionic acids having the substituents in the quinonoidal positions, which we have started, can provide further proofs of the correctness of the attempted interpretation or can cause the search for new explanation of the experimental data.

EXPERIMENTAL

The melting points are uncorrected. The IR and UV spectra were obtained in UNICAM SP-200 and SP-700 spectrophotometers. The ORD spectra were obtained by means of Perkin-Elmer 241-MC polarimeter, and the CD spectra – in Roussel Jouan III dichrograph. The compounds were examined in the form of suspensions in parraffin oil (IR) and in solutions quoted in the text.

1. 1,5-bromonaphthylacetic acid (1)

10 g (0.04 mole) of powered 1,5-bromo-cyanomethyl-naphthalene (prepared according to reference), m. p. 101–102°, lit. [6] m. p. 101–102°) was added to a solution of 8 g (0.2 mole) of KOH in 24 ccm of water and 12 ccm of 96% ethanol and the mixture was refluxed 8 hrs. on water bath. Ethanol was distilled off under reduced pressure (12 mm Hg, water bath) and the residue was treated with 250 ccm of water. The mixture was heated and was decolorized with bone charcoal. Then it was filtered and, after cooling to room temperature, acidified to Congo with dilute (1:1 V/V) hydrochloric acid. A fine crystalline precipitate immediately separated (7 g). It was filtered off and after washing with water (100 ccm), it was dried at room temperature. The crude acid (7 g) was crystallized from benzene (70 ccm). Colorless needles m. p. 166–167° (lit. [6] m. p. 164°). Yield 5 g. The compound is readilly soluble in acetone, methanol and 96% ethanol, and it is fairly soluble in benzene and carbon tetrachloride.

Analysis:

For the formula: $C_{12}H_9BrO_2$ (265.11) – calculated: 54.36% C, 3.42% H;
found: 54.45% C, 3.66% H.

IR (cm^{-1}): 690 νC–Br; 720, 780, 960, 1058, 1080, 1160 δC_{Ar}–H (subst. 1,2,3); 1460, 1500, 1585 $\nu C_{Ar}=C_{Ar}$; 940 δOH(COOH); 1210, 1300, 1420 δOH and νC–O(COOH); 1690 νC=O(COOH).

2. Amide of 1,5-bromonaphthylacetic acid (2)

2.65 g (0.01 mole) of powdered acid 1 was treated with 5 ccm of thionyl chloride and warmed 1 hr under a reflux condenser closed with a $CaCl_2$ tube. The excess of thionyl chloride was distilled off under reduced pressure (12 mm Hg, water bath at 45°). The oily residue was cooled with ice water and was treated with 30 ccm of 25% ammonia. The mixture was heated for 1.5 hr on steam bath. An amorphous precipitate separated. It was filtered and, after washing with water (2×15 ccm), crystallized from methanol (35 ccm). Colorless needles m. p. 223–224°. Yield 0.9 g. The compound is readlily soluble in dioxane, chloroform and acetone, and fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula $C_{12}H_{10}BrNO$ (264.11) – calculated: 5.35% N;
found: 5.37% N.

IR (cm^{-1}): 685 νC–Br; 715, 780, 975, 1058, 1085, 1180 δC_{Ar}–H (subst, 1,2,3); 1460, 1500, 1590 $\nu C_{Ar}=C_{Ar}$; 1400 νC–N; 1650 νC=O($CONH_2$); 1615 δNH and νC–N; 3150, 3350 νN–H.

3. Methyl ester of 1,5-bromonaphthylacetic acid (3)

2.65 g (0.01 mole) of acid 1 was suspended in 10 ccm of water and neutralized to phenolphthalein with 3% NaOH. Then 2.25 g (0.015 mole) of $AgNO_3$, dissolved in

30 ccm of water, was added. An amorphous precipitate immediately separated. The salt was filtered, washed with water (15 ccm) and 96% ethanol (30 ccm) and finally with anhydrous ether (50 ccm) and suspended in benzene (50 ccm). CH_3I (3.5 ccm) was added and the mixture was refluxed 4 hrs. under reflux condenser closed with $CaCl_2$ tube. AgI separated and was filtered off. Benzene was distilled off under reduced pressure (12 mm Hg, water bath). The oily residue soon solidified (1.7 g). It was crystallized from petroleum ether (10 ccm). Colorless plates m. p. 72–73°. Yield 0.9 g. The ester is very readily suluble in benzene, dioxane, chloroform, acetone, methanol and 96% ethanol. It is fairly soluble in petroleum ether.

Analysis:

For the formula: $C_{13}H_{11}BrO_2$ (279.13) – calculated: 55.93% C, 3.97% H;
found: 55.71% C, 3.71% H.

4. p-Nitrobenzyl ester of 1,5-bromonaphthylacetic acid (4)

2.65 g (0.01 mole) of acid 1 was suspended in 10 ccm of water and neutralized to phenolphthalein with 3% NaOH. The solution was heated to 60°, a few drops of 3% HCl was added (to make the solution slightly acid to litmus) and 2.16 g (0.01 mole) of p-nitrobenzyl bromide in 120 ccm of boiling methanol was added. The mixture was refluxed for 1 hr and filtered while it was still hot. A fine crystalline precipitate soon separated. It was filtered (3 g) and crystallized from methanol (85 ccm). Colorless needles m. p. 109–111°. Yield 2.1 g. The ester is readily soluble in dioxane, chloroform and acetone and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{19}H_{14}BrNO_4$ (400.21) – calculated: 3.50% N;
found: 3.72% N.

5. p-Bromophenacyl ester of 1,5-bromonaphthylacetic acid (5)

2.65 g (0.01 mole) of acid 1 was suspended in 10 ccm of water and converted into its sodium salt as in section 4. The solution of the salt was heated to 60° and treated with 2.78 g (0.01 mole) of p-bromophenacyl bromide in 130 ccm of hot methanol. The mixture was refluxed for 1 hr on water bath. It was filtered while being still hot and then was allowed to stand at room temperature. A colorless oil separated and soon solidified. It was filtered and after washing with water it was dried at room tenperature. The crude ester (3.1 g) was crystallized from methanol (125 ccm). Colorless needles m. p. 123–124°. Yield 1.9 g. The ester is very readily soluble in dioxane, chloroform and acetone and is fairly soluble in benzene, methanol and 96% ethanol.

Analysis:

For the formula: $C_{20}H_{14}Br_2O_3$ (462.13) – calculated: 51.97% C, 3.05% H;
found: 52.21% C, 2.90% H.

6. Racemic α-(1,5-bromonaphthyl)-propionic acid (6)

A solution of 10.24 g (0.08 mole) of naphthalene in 50 ccm of anhydrous tetrahydrofuran was placed in a three-necked round bottomed flask of 250 ccm capacity fitted with a stirrer (mercury seal), a reflux condenser closed with $CaCl_2$ tube and a dropping funnel. 1.84 g (0.08 mole) of sodium was added in small pieces. The mixture, which soon became dark green, was stirred for 3 hrs at room temperature and then a solution of 10.6 g (0.04 mole) of 1,5-bromonaphthylacetic acid in 50 ccm of dry ether was added dropwise during 30 min. The reaction was distinctly exothermic. Its temperature rose spontaneously to 38° and the mixture became pale yellow. In order to complete the reaction, the content of the flask was heated on water bath at 40° for 1.5 hrs. Then the mixture was cooled to 20° and 5.68 g (0.04 mole) of CH_3I in 20 ccm of dry ether was slowly added dropwise. The temperature of the mixture was kept at 36–38° (the reaction was exothermic). After introducing the whole amount of methyl iodide, the dense mass was stirred for 30 min. and after cooling to 15° it was poured into 400 ccm of water. The aqueous solution was extracted with ether (3×50 ccm). Ether dissolved in the alkaline solution removed by distillation under reduced pressure (12 mm Hg, water bath), and after decoloration with bone charcoal the solution was acidified to Congo with dilute (1:1 V/V) hydrochloric acid. An almost colorless oil separated and soon solidified. It was filtered and after washing with water (30 ccm) was dried at room temperature. The crude acid (6 g) was crystallized from benzene (35 ccm). Colorless plates m. p. 142.5–144°. Yield 4 g. The racemic acid is readily soluble in dioxane, acetone, methanol and 96% ethanol, fairly soluble in benzene, and sparingly soluble in petroleum ether.

Analysis:

For the formula: $C_{13}H_{11}BrO_2$ (279.13) – calculated: 55.93% C, 3.97% H;
found: 55.68% C, 3.72% H.

IR (cm^{-1}): 680 νC–Br; 710, 785, 975, 1060, 1080, 1155 δC_{Ar}–H (subst. 1,2,3); 1460, 1510, 1590, 1615 $\nu C_{Ar}=C_{Ar}$; 940 δOH(COOH); 1210, 1320, 1410 δOH and νC–O(COOH), 1695 νC=O(COOH).

7. Amide of racemic α-(1,5-bromonaphthyl)-propionic acid (7)

2.79 g (0.01 mole) of racemic acid 6 was converted into its amide as in section 2. The crude reaction product (2 g) was crystallized from methanol (20 ccm). Colorless needles m. p. 180–181°. Yield 1.2 g. The compound is readily soluble in chloroform, dioxane and acetone, and fairly soluble in benzene, methanol and 96% ethanol.

Analysis:

For the formula: $C_{13}H_{12}BrNO$ (278.15) – calculated: 5.04% N;
found: 5.28% N.

IR (cm^{-1}): 675 νC–Br; 710, 770, 980, 1060, 1080, 1195 δC_{Ar}–H (subst. 1,2,3); 1460, 1505, 1590 $\nu C_{Ar}=C_{Ar}$; 1420 νC–N; 1650 νC=O($CONH_2$); 1620 δN–H and νC–N; 3150, 3320 νN–H.

8. p-Nitrobenzyl ester of racemic α-(1,5-bromonaphthyl)-propionic acid (8)

2.79 g (0.01 mole) of racemic acid 6 was converted into its p-nitrobenzyl ester, as in section 4, using 2.16 g (0.01 mole) of p-nitrobenzyl bromide dissolved in 130 ccm of methanol. The crude ester (2.9) was crystallized from methanol (90 ccm). Pale yellow plates m. p. 114–115°. Yield 2 g. The compound is readily soluble in benzene, dioxane and chloroform, and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{20}H_{16}BrNO_4$ (414.25) – calculated: 3.38% N;
found: 3.49% N.

9. p-Bromophenacyl ester of racemic α-(1,5-bromonaphthyl)-propionic acid (9)

2.79 g (0.01 mole) of racemic acid 6 was converted into its p-bromophenacyl ester, as in section 5, using 2.78 g (0.01 mole) of p-bromophenacyl bromide dissolved in 80 ccm of methanol. The crude reaction product (2.8 g) was crystallized from methanol (65 ccm). Colorless needles m. p. 119.5–120.5°. Yield 1.8 g. The compound is readily soluble in benzene, chloroform, dioxane and acetone, and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{21}H_{16}Br_2O_3$ (476.17) – calculated: 52.97% C, 3.39% H;
found: 52.79% C, 3.41% H.

10. Brucine salt of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid (10)

20 g (0.07 mole) of powdered acid 6 was mixed with 28.26 g (0.07 mole) of brucine and the mixture was dissolved in 1.3 l of boiling acetone. The hot solution was fitered and was allowed to stand at room temperature for crystallization. After 24 hrs. the first fraction of the salt was filtered off. Colorless rods m. p. 143–144°, $[\alpha]_D^{20} = -36.0°$ (c = = 0.5, d = 2, $\alpha = -0.36°$) in acetone. After three crystallizations of the first fraction of the salt its physical properties did not change on further crystallization. Colorless rods, m. p. 144–145°, $[\alpha]_D^{20} = -20.0°$ (c = 0.5, d = 2, $\alpha = -0.20°$) in acetone. Yield 8.5 g. The salt is readily soluble in benzene and chloroform, and is fairly soluble in acetone, methanol and 96% ethanol.

Analysis:

For the formula: $C_{36}H_{27}BrN_2O_6$ (653.58) – calculated: 4.16% N;
found: 4.45% N.

Table 6. Fractional crystallization of brucine salt of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid. Crystallization time 24 hrs

Fraction No.	Vol. of acetone (ccm)	Weight of salt (g)	Specyfic rotation in acetone $[\alpha]_D^{20}$	M. p. of the salt °C
1.	1300	20.8	−36.0°	143–144
1.1.	890	13.1	−27.0°	143–144
1.1.1.	630	10.8	−20.0°	144–145
1.1.1.1.	500	8.5	−20.0°	144–145

11. Dextrorotatory α-(1,5-bromonaphthyl)-propionic acid (11)

8.1 g (0.012 mole) of powered brucine salt 10 (m. p. 144–145, $[\alpha]_D^{20} = -20.0°$) was suspended in 80 ccm of water, 50 ccm of 3% NaOH was added and the mixture was stirred for 30 min. on water bath at 45°. Liberated brucine was filtered off and the filtrate was extracted with chloroform (5×30 ccm). Chloroform dissolved in the alkaline liquid was distilled off under reduced pressure (12 mm Hg, water bath at 45°) and the residue was acidified to Congo with 3% HCl. A colorless oil separated and soon solidified. It was filtered and after washing water (2×30 ccm) dried in a vacuum desiccator over $CaCl_2$. The crude acid (3.2 g) was crystallized from a mixture of petroleum ether (40 ccm) and benzene (20 ccm). Colorless plates, m. p. 127–128°, $[\alpha]_D^{20} = +53.0°$ ($c = 0.5, d = 2, \alpha = +0.53°$) in 96% ethanol. The compound is very readily soluble in benzene, dioxane, chloroform, acetone, methanol and 96% ethanol, and is sparingly soluble in petroleum ether.

Analysis:

For the formula: $C_{13}H_{11}BrO_2$ (279.11) – calculated: 55.93% C, 3.97% H;
found: 55.65% C, 4.23% H.

IR (cm^{-1}): 680 νC–Br; 710, 780, 985, 1075, 1085, 1170 δC_{Ar}–H (subst. 1,2,3); 1455, 1506, 1585, 1600 $\nu C_{Ar}=C_{Ar}$; 940 δOH(COOH); 1235, 1320, 1420 δOH and νC–O(COOH); 1685 and 1718 νC=O(COOH).

12. Cinchonidine salt of laevorotatory α-(1,5-bromonaphthyl)-propionic acid (12)

20 g (0.07 mole) of powdered acid 6 was mixed with 20.51 g (0.07 mole) of cinchonidine and the mixture was dissolved in 420 ccm of boiling acetone. The hot solution was filtered and allowed to stand at room temperature for crystallization. After 24 hrs. the first fraction of the salt was filtered off. Colorless needles (21 g), m. p. 135–137°, $[\alpha]_D^{20} = -61.0°$ ($c = 0.5, d = 2, \alpha = -0.61°$) in acetone. After three crystallizations of the first fraction from acetone, the physical properties and the melting point of the product did

Table 7. Fractional crystallization of cinchonidine salt of laevorotatory α-(1,5-bromonaphthyl)-propionic acid. Crystallization time 24 hrs

Fraction No.	Vol. of acetone (ccm)	Weight of salt (g)	Specyfic rotation in acetone $[\alpha]_D^{20}$	M. p. of the salt °C
1.	420	21.0	−61.0°	135–137
1.1.	380	16.5	−71.0°	137–140
1.1.1.	370	12.9	−79.0°	139–142
1.1.1.1.	290	10.8	−81.0°	141–143
1.1.1.1.1.	250	9.0	−81.0°	141–143

not change any more on further crystallization. Colorless needles, m. p. 141–143°, $[\alpha]_D^{20} = -81.0°$ ($c = 0.5, d = 2, \alpha = -0.81$) in acetone. Yield 9 g. The salt is readily soluble in dioxane and chloroform, and is fairly soluble in acetone, methanol and 96% ethanol.

Analysis:

For the formula: $C_{32}H_{33}BrNO_3$ (573.51) – calculated: 4.88% N;
found: 5.12% N.

13. Laevotorotatory α-(1,5-bromonaphthyl)-propionic acid (13)

8.5 g (0.015 mole) of powdered cinchonidine salt 12 (m. p. 141–143°, $[\alpha]_D^{20} = -81.0°$) was suspended in 100 ccm of water and 3% NaOH (50 ccm) was added with stirring. The mixture together with the separating alkaloid was stirred for 30 min. on water bath at 40–45°. Cinchonidine was filtered off and the filtrate was extracted (5×30 ccm) with chloroform. Chloroform dissolved in the alkaline liquid was distilled off under reduced pressure (12 mm Hg, water bath at 45°) and the residue was acidified to Congo with 3% hydrochloric acid. A colorless oil separated and soon solidified. It was filtered and after washing with water (2×25 ccm) it was dried in a vacuum desiccator over $CaCl_2$. The crude acid (3.8 g) was crystallized from a mixture of benzene (25 ccm) and petroleum ether (50 ccm). Colorless rods, m. p. 127–128°, $[\alpha]_D^{20} = -54.0°$ ($c = 0.5, d = 2, \alpha = -0.54°$) in 96% ethanol. The compound is very readily soluble in benzene, dioxane, chloroform, acetone, methanol and 96% ethanol, and is sparingly soluble in petroleum ether.

Analysis:

For the formula: $C_{13}H_{11}BrO_2$ (279.13) – calculated: 55.93% C, 3.97% H;
found: 55.81% C, 4.06% H.

14. Amide of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid (14)

2 g (0.007 mole) of powdered acid 11 (m. p. 127–128°, $[\alpha]_D^{20} = +53.0°$ in 96% ethanol) was converted into its acid chloride, as in section 2, using 6 ccm of $SOCl_2$. The oily residue after the removal of the excess of thionyl chloride, in a vacuum desiccator over KOH, was cooled with ice water and treated with 30 ccm of 25% ammonia. The mixture was heated for 30 min. on steam bath. The reaction product (1.3 g) was filtered and, after washing with water (2×20 ccm), crystallized from methanol (20 ccm). Colorless needles, m. p. 180°, $[\alpha]_D^{20} = +29.0°$ ($c = 0.5$, $d = 2$, $\alpha = +0.29°$) in 96% ethanol. Yield 0.9 g. The compound is readily soluble in dioxane, chloroform and acetone, and is fairly soluble in benzene, methanol and 96% ethanol.

Analysis:

For the formula: $C_{13}H_{12}BrNO$ (278.15) – calculated: 5.04% N;
found: 5.24% N.

IR (cm^{-1}) 665 νC–Br; 718, 780, 975, 1060, 1080, 1160 δC_{Ar}–H (subst. 1,2,3); 1460, 1510, 1565, 1600 $\nu C_{Ar}=C_{Ar}$; 1400 νC–N; 1635 νC=O($CONH_2$); 1615 δN–H and νC–N, 3190, 3350 νN–H.

15. p-Nitrobenzyl ester of dextrorotatory α-(1,5-bromonaphthyl)-propionic acid (15)

2.79 g (0.01 mole) of acid 11 (m. p. 127–128°, $[\alpha]_D^{20} = +53.0°$ in 96% ethanol) was converted into its sodium salt as in section 4. To warm (50°) solution of the sodium salt 2.16 g (0.01 mole) of p-nitrobenzyl bromide, dissolved in 80 ccm of boiling methanol, was added, and the mixture was refluxed for 1 hr. on water bath. Then it was filtered, when still hot and allowed to stand at room temperature. A cream colored oil separated. After 24 hrs. it solidified. It was filtered and dissolved in diethyl ether. The solution was washed successively with 3% $NaHCO_3$ (2×20 ccm) and water (2×40 ccm) and was dried with anhydrous $MgSO_4$. The solvent was dislilled of under reduced pressure (12 mm Hg, water bath), and the solid residue (2.4 g) was crystallized from methanol. Pale yellow rods, m. p. 97–98°, $[\alpha]_D^{20} = +73.0°$ ($c = 0.5$, $d = 2$, $\alpha = +0.365$) in 96% ethanol. Yield 1.7 g. The compound is readily soluble in benzene, chloroform, dioxane and acetone, and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{20}H_{16}BrNO_4$ (414.25) – calculated: 3.38% N;
found: 3.35% N.

REFERENCES

1. Janczewski M., Stankiewicz G.: Ann. Univ. Mariae Curie-Skłodowska, Lublin, sectio AA, 23 (2), 5 (1968).
2. Janczewski M., Kut K., Jabłońska T.: Roczniki Chem. 44, 563 (1970).
3. Janczewski M., Jabłońska-Pikus T.: Pol. J. Chem., 54, 1155 (1980).

4. Ruggi P., Preuss P.: Helv. Chim. Acta 24, 1345 (1941).
5. Schoesmith B., Rubli H.: J. Chem. Soc. 1927, 3102.
6. Dizabo P., Mouneyrac M.: Bull. soc. chim. France, (1968), 2957.
7. Fredga A.: Arkiv. Kemi 8, 463 (1955).
8. Janczewski M., Maziarczyk H.: Roczniki Chem. 42, 657 (1968).
9. Korver O.: Tetrahedron 26, 5507 (1970).
10. Janczewski M.: Roczniki Chem. 35, 601 (1961).
11. Janczewski M., Bartnik T.: Roczniki Chem. 40, 1919 (1966); 42, 1253 (1968).

STRESZCZENIE

Problem wpływu izomerii położenia atomu halogenu w pierścieniu arenowym na własności optyczne połączeń aromatyczno-tłuszczowych z węglowymi ośrodkami chiralności studiowany był ostatnio w naszej pracowni na przykładzie bromowych pochodnych kwasów α-(1- i 2-naftylo)-propionowych. W poprzednich doniesieniach opisana została synteza oraz podstawowe własności fizyczne optycznie czynnych kwasów α-(1-naftylo)-propionowych [1], jak również ich kata- [3] i para- [2] -bromopochodnych. Zaobserwowane prawidłowości optyczne zachęciły nas do rozszerzenia studiów.

Przedmiotem bieżącego doniesienia są wyniki badań związanych z opracowaniem syntezy oraz określeniem podstawowych własności optycznych i stereochemicznych enancjomerycznych kwasów α-(1,5-bromonaftylo)-propionowych.

Związkiem wyjściowym był 1-naftaldehyd, który po zbromowaniu w położeniu 5, zredukowaliśmy do 1,5-bromohydroksymetylonaftalenu. Karbinol przerobiony został na 1,5-bromo-bromometylonaftalen, którego przemiana na bromo-cyjanometylo-naftalen zachodziła z dość dobrą wydajnością. Hydroliza nitrylu do wolnego kwasu 1,5-bromonaftylooctowego (1) przeprowadzona została roztworem ługu potasowego w środowisku rozc. etanolu. Poszukiwany rac. kwas α-(1,5-bromonaftylo)-propionowy (6) otrzymaliśmy w toku metylowania kwasu 1 jodkiem metylu w obecności sodonaftalenu w bezw. eterze dwuetylowym.

Rac. kwas 6 rozszczepiliśmy na enancjomery optyczne metodą krystalizacji związków diastereomerycznych uzyskanych przez wiązanie kwasu optycznie biernego z brucyną i cinchonidyną. Optycznie czynne kwasy 11 i 13 wykazywały stosunkowo niskie skręcalności właściwe $[\alpha]_D^{20} = \pm 53{,}0°$ (etanol). Zaobserwowane różnice między widmami oscylacyjnymi antypodu (11 i 13) i kwasu racemicznego (6) wskazywały, że ten ostatni stanowi układ prawdziwego racematu.

Problem określenia konfiguracji przestrzennych enancjomerycznych kwasów α-(1,5-bromonaftylo)-propionowych (11 i 13) rozwiązany został w oparciu o prawo przesunięć Freudenberga oraz na podstawie obserwacji kierunku zmian rotacji cząsteczkowych występujących pod wpływem odpowiednio dobranej serii rozpuszczalników przy zastosowaniu w obu przypadkach optycznie czynnych kwasów α-(1-naftylo)-propionowych, jako wzorców konfiguracyjnych. Na podstawie przeprowadzonych korelacji prawoskrętnemu kwasowi α-(1,5-bromonaftylo)-propionowemu przypisaliśmy konfigurację S(+).

Celem uzyskania dostatecznie obszernego materiału porównawczego do badań chiralooptycznych przyrządziliśmy amid (14) oraz ester p-nitrobenzylowy (15) prawoskrętnego kwasu α-(1,5-bromonaftylo)-propionowego (11). Oznaczenia skręcalności molowych prawoskrętnego kwasu 11 oraz jego pochodnych 14 i 15 wykonane zostały w metanolu (M), etanolu (E), acetonie (A), dioksanie (D) i chloroformie (Ch) w rejonie $600 < \lambda < 300$ nm. Uzyskane wyniki podano w tab. 1. Zależności rotacji molowych od długości fal świetlnych w widzialnej części widma, można opisać w przybliżeniu jednotermowym równaniem Drudego. Aby przeanalizować własności chiralooptyczne wolnych kwasów α-(1,5-bromonaftylo)-propionowych w szerszym zakresie widmowym, wyznaczyliśmy na podstawie zebranego w tab. 1 materiału liczbowego ($300 < \lambda < 600$ nm) funkcję $[M](\lambda)$ dla enancjomeru prawoskrętnego w czterech rozpuszczalnikach oraz określiliśmy widma UV i CD w rejonie $200 < \lambda < 600$ nm. Wyznaczone funkcje $[M](\lambda)$ mają charakter trójtermowych równań. Zgodność wartości obliczonych z wyznaczonymi doświadczalnie jest dobra.

Studiowane obecnie kwasy ana α-(bromonaftylo)-propionowe, ich amidy i estry p-nitrobenzylowe wykazują w rejonach widmowych o dyspersji normalnej (widzialna część widma) we wszystkich stosowanych do pomiarów rozpuszczalnikach znacznie mniejsze wartości numeryczne rotacji molowych aniżeli odpowiadające im układy nie podstawione halogenem w pierścieniu naftalenowym. Nie jest wykluczone, że zaobserwowane zmniejszenie się rotacji molowych może mieć pewien wpływ oddziaływanie efektów indukcyjnego i mezomerycznego, wzbudzonych przez wprowadzony podstawnik, na swobodne naboje pierścienia arenowego.

РЕЗЮМЕ

Проблема влияния изомерии положения атома галогена в ареновом кольце на оптические свойства ароматическо-жирных соединений с угольными центрами хиральности рассматривалась в последнее время в нашей лаборатории на примере бромовых производных α-(1 и 2-нафтило)-пропионовых кислот. В предыдущих работах был описан синтез и основные физические свойства оптически деятельных α-(-1-нафтило)-пропионовых кислот [1], а также их ката [3] и пара [2] бромопроизводных. Увлеченные оптическими регулярностями, авторы расширили исследования.

Предметом данной работы являются результаты исследований связанных с обработкой синтеза и определением основных оптических и стереохимических свойств энанциомарических α-(1,5-бромонафтило)-пропионовых кислот.

Выходящим соединением был 1-нафталдегид, который после бромирования в позиции 5, восстановили до 1,5-бромогидроксиметило-нафталена. Карбинол был переработан на 1,5-бромо-бромометило-нафтален, перемена которого на бромо--цианометило-нафтален проходила с очень хорошой производительностью. Гидролиз нитрила до свободной 1,5-бромонатилоуксусной кислоты (1) проведен раствором калийного щелка в среде разв. этанола. Рацемическую α-(1,5,-бромонафтило)-пропионовую кислоту (6) получили в ходе метилирования кислоты 1 йодистым метилом в присутствии сода нафталена в безв. диэтиловом эфире.

Рац. 6 кислоту расщепили на оптические энанциомеры методом кристаллизации диастереомерических соединений полученных путем связывания оптически пассивной кислоты с бруцином и цинхонидином. Оптически деятельные кислоты 11 и 12 проявляли относительно небольшие оптические вращения, специфические для $[\alpha]_D^{20} = \pm 53{,}0°$ (этанол). Замеченные разницы выступающие между спектрами колебаний антиподов [11 и 13] и рацемической кислотой (6) показали, что кислота является расположением настоящего рацемата.

Проблема определения пространственной конфигурации энанциомерических α-(1,5-бромонафтило)-пропионовых (11 и 13) кислот была решена опираясь на закон смещения Фройденберга, а также на основе наблюдения направления изменений молярного вращения, выступающих под влиянием соответственно подобранной серии растворителей, применяя в обоих случаях оптически деятельных α(1-нафтило)-пропионовых кислот, как конфигурационных эталонов. На основе проведенной корреляции, правовращающей α-(1,5-бромонафтило)-пропионовой кислоте приписано конфигурацию S(+).

Для получения достаточно обширного сопоставительного материала для хиралооптических исследований, изготовлено амид (14) и р-нитробензиловый эстер (15), правовращающей α-(1,5-бромонафтило)-пропионовой кислоты. Определение мольного вращения правовращающей кислоты 11 и ее производных 14 и 15 изготовлены в метаноле (M), этаноле (E), ацетоне (A), диоксане (D) и хлороформе

(Ch), в $600 \leq \lambda \leq 300$ nm. Полученные результаты представлено в табл. 1. Зависимости мольного вращения от длины световой волны в видимой части спектра, можно описать приблизительно однотермным уравнением Друге. Чтобы проанализировать хиралооптические свойства свободных α-(1,5-бромонафтило)-пропионовых кислот в широком спектральном диапазоне, было определено на основе собранного в табл. 1 числового материала ($300 < \lambda < 600$) функции [M] (λ) для правовращающего энанциомера в четырех растворителях, а также определено UV и CD спектры в $200 < \lambda < 600$. Определенные функции [M] (λ) имеют тритермный характер уравнений. Соотношение подсчитанных величин с величинами представленными опытами хорошое.

Исследованные ана-α-(бромонафтило)-пропионовые кислоты, их амиды и п-нитробензиловые эстры показывают в спектральных районах с нормальной дисперсией (видимая часть спектра) при всех применяемых для измерения растворителях значительно меньшее нумерические величины мольных вращений, чем отвечающие им системы не подставлены галогеном в нафталеновом кольце. Не исключается, что на замеченное уменьшение мольных вращений может иметь влияние воздействие индукцийного и мезомерического эффектов, которые были возбуждены введенным заместителем на свободные заряды аренового кольца.