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Effect of Molecular Structure on Optical Properties
of Systems Containing Carbon Chirality Centers.

9,9-Methyl-Propyl-Fluorene-2-Carboxylic Acids and Some of Their Derivatives.* XXII

Wpływ budowy cząsteczkowej na własności optyczne układów z węglowymi centrami chiralności.
Kwasy 9,9-metylo-propylo-fluoreno-2-karboksyłowe i niektóre ich pochodne. XXII

Влияние молекулярного строения на оптические свойства расположений с углеродными центрами хиральности. 9,9-метило-пропило-флюрено-2-карбоксыловые кислоты и их производные. XXII

Optical relationships in homologous series of systems containing carbon chirality centers with restricted rotation were studied in our laboratory only in the group of 9-methyl, ethyl and propyl-fluorene-2-carboxylic acids [1]. In these studies we have found that the compounds rotating the plane of polarized light in the visible part of the spectrum in the same direction have the same configurations and that the dependence of molar rotation of the free acids in the ultraviolet and visible parts of the spectrum on wave length can be described by two-term equations. We have also found that in the region $480 < \lambda < 613$ nm functions $1/\alpha(\lambda^2)$ are approximately linear and that in this region the molar rotation of homologous 9-alkylfluorene-2-carboxylic acids, in the solvents used in our experiments, increases with increasing substituent in position 9 of the fluorene ring. Although our observations are not in disagreement with the classical Chugaev's rules, it should be stressed that $[M]_{\lambda}^t(M)$ functions corresponding to the systems studied by Chugaev and to alkylfluorenes studied by us do not show the expected similarities.

In order to obtain further experimental material for our studies, including compounds more resistant to racemization than the previously studied ones, we have decided to

* Preliminary communication: Janczewski M., Pawłowska E.: Roczniki Chem. 47, 665 (1973).

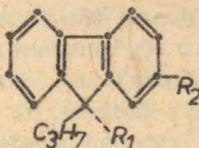
investigate the homologous series of 9,9-methyl-alkylfluorene-2-carboxylic acids. The principal chiroptical properties of the first member of the series, i.e. 9,9-methyl-ethyl-fluorene-2-carboxylic acid, were described in our previous publication [2].

In the present paper we describe the synthesis of racemic 9,9-methyl-propyl-fluorene-2-carboxylic acid (4), its resolution and the principal chiroptical properties of its laevorotatory antimer, its esters and amides.

The starting material was 9,9-methyl-propyl-fluorene (2) which we obtained by the action of methyl iodide on sodium derivative of 9-propyl-fluorene (1). Then we acetylated compound 2 and we obtained a fairly good yield of 9,9-methyl-propyl-2-acetyl-fluorene (3). The structure of acetyl derivatives of 9,9-dialkyl-fluorenes had been proved in our laboratory earlier [2]. We obtained racemic 9-methyl-propyl-fluorene-2-carboxylic acid (4), which is a new compound, by oxidation of ketone 3 with sodium hypobromite in dilute dioxane. The structure of 4 was fully confirmed by elemental analysis and IR spectra (the characteristic bands are given in the Experimental Part). Racemic acid 4 gave readily crystallizing amides 5, 6 and 7 and esters 8 and 9.

In our further work we have resolved racemic acid 4 by crystallization of its diastereometric compounds with optically active alkaloids. We obtained the best results using brucine and cinchonidine. The salts with other alkaloids could be readily prepared and crystallized fairly well but were unsuitable for rapid separation for the antimers. The brucine salt of the laevorotatory antimer was much less soluble in dilute ethanol than that of the dextrorotatory one, which made it possible to separate the antimers very readily. The optically homogeneous salt of the laevorotatory acid 12 had m. p. 104–106° with decompn. and $[\alpha]_D^{20} = -25.8^\circ$ (methanol). The equimolar salt of cinchonidine with acid 4 was crystallized from moist acetone and gave the dextrorotatory enantiomer in the front fractions. The optically homogeneous salt 10 had m. p. 169–170° with decompn. and $[\alpha]_D^{20} = -47.5^\circ$ (methanol).

The optically active 9,9-methyl-propyl-fluorene-2-carboxylic acids 11 and 13 freed in



- | | |
|--|---|
| 1: $R_1 = H, R_2 = H$ | 10: $R_1 = CH_3, R_2 = COOH \cdot Cinchnd.*$ |
| 2: $R_1 = CH_3, R_2 = H$ | 11: $R_1 = CH_3, R_2 = COOH(+)$ |
| 3: $R_1 = CH_3, R_2 = COCH_3$ | 12: $R_1 = CH_3, R_2 = COOH \cdot Bruc.**$ |
| 4: $R_1 = CH_3, R_2 = CO \cdot OH$ | 13: $R_1 = CH_3, R_2 = COOH(-)$ |
| 5: $R_1 = CH_3, R_2 = CO \cdot NH_2$ | 14: $R_1 = CH_3, R_2 = CO \cdot NH_2(-)$ |
| 6: $R_1 = CH_3, R_2 = CO \cdot NH \cdot CH_3$ | 15: $R_1 = CH_3, R_2 = CO \cdot NH \cdot CH_3(-)$ |
| 7: $R_1 = CH_3, R_2 = CS \cdot NH \cdot CH_3$ | 16: $R_1 = CH_3, R_2 = CS \cdot NH \cdot CH_3(-)$ |
| 8: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4 \cdot Br$ | 17: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4Br(-)$ |
| 9: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot C_6H_4 \cdot NO_2$ | |

* Cinchnd. = cinchonidine.

** Bruc. = brucine.

the usual way from the alkaloids and crystallized from dilute ethanol had relatively low specific rotations ($[\alpha]_D^{20} = -35.2^\circ$ and $+35.0^\circ$ (methanol)). They were very resistant to racemization.

A mixture of equimolar amounts of the antimers after crystallization gave racemic acid 4. Its m. p. is much higher ($\Delta t = 47^\circ$) than that of the antipodes 11 and 13. The IR spectrum of racemic acid 4 shows in the "finger print" region differences from the spectra of enantiomers 11 and 13 which are identical. The physical differences between the antipodes and the racemate and the relatively difficult resolution of acid 4 indicate that the latter is a true racemate.

In order to obtain further comparable material for chiroptical studies we have prepared the following derivatives of laevorotatory acid 13: amide 14, methylamide 15, methylthioamide 16 and p-bromophenacyl ester 17. The syntheses of these compounds were first tried on the optically inactive material. The mild conditions of the syntheses exclude the possibility of racemization at the asymmetric carbon atom. We have determined the molar rotations of laevorotatory acid 13, its amide 14 and p-bromophenacyl ester 17 in Perkin-Elmer 241-MC spectropolarimeter in ethanol (E), chloroform (Ch), tetrahydrofuran (THF) and dimethylformamide (DMF). The results are shown in Table 1.

Comparison of the data shown in Table 1 indicates that the molar rotations of acid 13 and its p-bromophenacyl ester 17 depend considerably on the character of the solvent. In the visible part of the spectrum the solvent effect can be represented by the following sequences: a) for the free acid: $E > Ch > DMF > THF$; b) for p-bromophenacyl ester: $E > THF > Ch > DMF$ (in the order of decreasing values of molar rotation). The decreases of molar rotation accompanying the changes of solvents according to the above sequences are moderate.

The analysis of the data shown in Table 1 indicates that for acid 13 and its amide 14 function $(1/\alpha)(\lambda^2)$ in the region $436 < \lambda < 623$ nm is almost linear, which leads to the conclusion that the optical rotatory dispersion of the examined compounds in the visible part of the spectrum is normal.

In the previous communication we proved homologous 9-methyl-ethyl- and propyl-fluorene-2-carboxylic acids, rotating the plane of visible polarised light in the same direction, have the same configurations [1]. We did not think that slight changes at the chirality center could cause radical configurational changes. In order to check this hypothesis we have compared the configurations of the previously described compounds with those of the compounds prepared in the present work. The comparison could not be carried out by the classical methods since the optical shifts of the simplest derivatives of the examined acids were small and only partly solvent dependent. In addition, the mono-substituted derivatives had no tendency to the formation of true racemate. For this reason we have carried out the comparison using ORD and CD curves of methylthioamides of laevorotatory 9-methyl-fluorene-2-carboxylic and 9,9-methyl-propyl-fluorene-2-carboxylic acids.

The rotation and dichroic curves of these amides have analogous structures in 96% ethanol. The ORD curve of methylthioamide of laevorotatory 9-methyl-fluorene-2-carboxylic acid has a minimum at $\lambda = 410$ nm where $[M]_{410}^{20} = -1344.3^\circ$ and at $\lambda = 367$ nm the ORD curve cuts the λ axis, whereas the CD curve has a negative maximum at $\lambda = 365$ nm

Tab. 1. Rotatory dispersion of laevorotatory 9,9-methyl

Compound	Solvent	Concn.	Molar rotation $[M]_{\lambda}^{20}$		
		g/100 ccm	$\lambda=600$ nm	$\lambda=589$ nm	$\lambda=560$ nm
Laevorotatory 9,9-methylpropyl-fluorene-2-carboxylic acid	E	0.40	91.9 (86.9)	93.2 (91.2)	105.1 (103.8)
	Ch	0.20	77.2 (78.0)	79.9 (81.8)	93.2 (93.5)
	THF	0.205	67.9 (68.4)	71.1 (71.7)	81.8 (81.9)
	DMF	0.245	76.1 (75.9)	79.4 (79.6)	91.3 (90.7)
Laevorotatory 9,9-methylpropyl-fluorene-2-carboxylic acid amide	E	0.19	98.6	104.2	118.1
	Ch	0.249	81.9	85.2	95.8
	THF	0.41	78.9	82.2	97.1
	DMF	0.40	75.6	84.9	94.2
p-bromophenacyl ester of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid	E	0.102	109.0	113.6	136.3
	Ch	0.20	97.3	99.6	115.8
	THF	0.20	106.6	111.2	132.0
	DMF	0.20	87.9	92.7	104.3

E – ethanol, Ch – chloroform, THF – tetrahydrofuran, DMF – dimethylformamide.

where $[\Theta]_{365}^{20} = -710.4$. Analogously on the curves of methylthioamide of laevorotatory enantiomer 13 there is a minimum at $\lambda = 404$ nm where $[M]_{404}^{20} = -200893.8^{\circ}$ (at $\lambda = 368$ nm the ORD curve cuts the λ axis), and at $\lambda = 366$ nm there is a negative dichroic maximum having $[\Theta]_{366}^{20} = -41735.3$. The determination of the extrema of the ORD and CD curves at shorter wave lengths was not possible probably as a result of the background effect [3] of the $\Pi \rightarrow \Pi^*$ bands.

The above experimental facts indicate that the enantiometric 9-methyl- and 9,9-methyl-propyl-fluoreno-2-carboxylic acids rotating the plane of polarised light in the same direction have the same configurations.

The UV spectra (obtained in 96% ethanol) of the methylthioamides [1] of laevorotatory antimers are also very similar (the spectrum of enantiomer 13 is given in the Experimental Part). It should be noted that the molar extinction coefficients in the region 200–335 nm are high. The band of methylthioamide 16 at $\lambda = 353$ nm ($\epsilon_{353} = 3065.1$) is probably the optically active band corresponding to the $n \rightarrow \Pi^*$ transition of the thioamide group (thioamides of aliphatic acids show selective absorption in the region 325–350 nm and the molar extinction coefficients of the bands localized in this region are low [3, 4]).

The dependence of molar rotations of laevorotatory acid 13 and its amide 14 on polarized light wave length in ethanol, chloroform, tetrahydrofuran and dimethylformamide can be described by the following two-term equations*:

Acid 13:

a) in ethanol:

* The two-term equations were derived by the least squares method using digital computer ODRA-1013.

propylfluorene-2-carboxylic acid and of some of its derivatives

Molar rotation $[M]_{\lambda}^{20}$							
$\lambda=520$ nm	$\lambda=480$ nm	$\lambda=450$ nm	$\lambda=435$ nm	$\lambda=400$ nm	$\lambda=380$ nm	$\lambda=360$ nm	$\lambda=340$ nm
130.4 (127.0)	155.8 (160.2)	191.1 (196.1)	214.5 (215.7)	323.7 —	420.1 (424.3)	487.4 (490.1)	704.4 (705.5)
114.5 (114.5)	146.5 (145.9)	181.0 (180.0)	203.7 (202.9)	282.3 (282.9)	360.9 (361.1)	494.0 (495.6)	—
100.0 (100.2)	127.2 (126.6)	155.9 (155.3)	174.0 (174.1)	239.0 (138.5)	298.8 (298.5)	394.9 (394.6)	576.8 (576.8)
110.8 (110.8)	139.2 (139.7)	170.7 (170.9)	192.4 (191.4)	266.4 (260.9)	325.0 (325.4)	426.7 (427.9)	621.2 (621.3)
144.5	181.9	222.3	248.7	338.9	420.9	544.6	783.5
116.1	143.7	174.6	192.8	270.5	330.1	436.6	643.1
119.1	148.2	180.6	201.3	271.8	337.8	438.8	621.3
106.1	145.9	179.1	200.3	270.6	333.0	428.5	508.9
145.4	206.7	254.4	286.2	404.3	513.3	704.1	—
141.3	180.7	224.7	252.5	361.4	465.7	657.9	1065.7
157.5	199.2	240.9	271.0	375.3	474.9	625.5	973.0
132.0	166.8	210.8	236.3	331.3	421.7	579.2	834.0

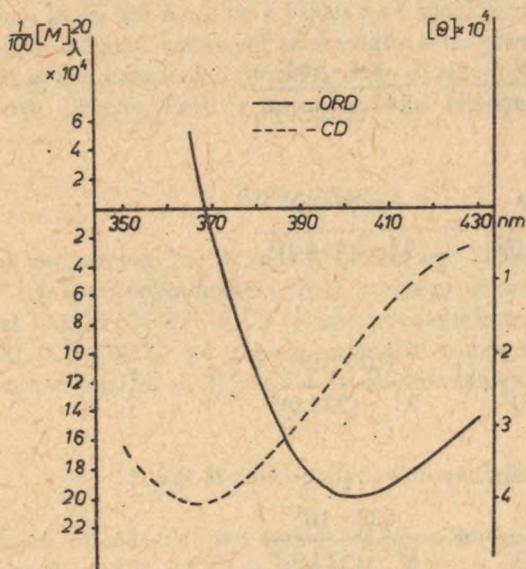


Fig. 1. Optical rotatory dispersion (ORD) and circular dichroism (CD) of methylthioamide of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid in 96% ethanol

ORD $c = 0.001$ g/100 cm³, $d = 0.05$ dcm; tr ; $[M]_{404}^{20}$ nm = -200893.8° ($\alpha = -0.0340$), $[M]_{360}^{20}$ nm = 0.0 ($\alpha = 0.0^{\circ}$).

CD $c = 0.0006769$ mole/dcm³, $d = 0.1$ cm ($[\theta]_{360}^{20}$ nm = -41735.3 ($\Delta A = 0.00086$)).

$$|[M]_{\lambda}^{20}| = \frac{160 \cdot 10^5}{\lambda^2 - (296.5)^2} + \frac{882 \cdot 10^4}{\lambda^2 - (218.1)^2}$$

b) in chloroform:

$$|[M]_{\lambda}^{20}| = \frac{130 \cdot 10^5}{\lambda^2 - (309.7)^2} + \frac{902 \cdot 10^4}{\lambda^2 - (218.6)^2}$$

c) in tetrahydrofuran:

$$|[M]_{\lambda}^{20}| = \frac{124 \cdot 10^5}{\lambda^2 - (298.9)^2} + \frac{701 \cdot 10^4}{\lambda^2 - (218.7)^2}$$

d) in dimethylformamide:

$$|[M]_{\lambda}^{20}| = \frac{128 \cdot 10^5}{\lambda^2 - (299.2)^2} + \frac{896 \cdot 10^4}{\lambda^2 - (219.0)^2}$$

amide 14:

a) in methanol:

$$|[M]_{\lambda}^{20}| = \frac{161 \cdot 10^5}{\lambda^2 - (297.7)^2} + \frac{125 \cdot 10^5}{\lambda^2 - (222.0)^2}$$

b) in chloroform:

$$|[M]_{\lambda}^{20}| = \frac{983 \cdot 10^4}{\lambda^2 - (306.0)^2} + \frac{135 \cdot 10^5}{\lambda^2 - (216.2)^2}$$

c) in tetrahydrofuran:

$$|[M]_{\lambda}^{20}| = \frac{130 \cdot 10^5}{\lambda^2 - (296.2)^2} + \frac{102 \cdot 10^5}{\lambda^2 - (223.0)^2}$$

d) in dimethylformamide:

$$|[M]_{\lambda}^{20}| = \frac{144 \cdot 10^5}{\lambda^2 - (293.0)^2} + \frac{833 \cdot 10^4}{\lambda^2 - (220.0)^2}$$

The molar rotations calculated on the basis of the above equations are given (in brackets) in the Table. The agreement between the calculated and the experimentally determined values is very good.

Functions $(M)(\lambda)$ describing the optical properties of acid 13 do not change the sign in

the range $\lambda_2 < \lambda < \lambda_1$, have no inflexion points and no extreme values. The asymptotes of these functions are the λ axis and the straight lines perpendicular to it at points $\lambda = \lambda_1$ and $\lambda = \lambda_2$. According to the classical Lowry's definitions the optical rotatory dispersion expressed by the above equations could be called "complex but normal".

In order to check that the dispersion constants of the two-term equations describing the optical rotation of 9,9-methyl-propyl-fluorene-2-carboxylic acid are in agreement with the UV spectrum, we have measured the adsorption in ultraviolet of laevorotatory acid 13 in ethanol. The UV spectrum of this acid has two groups of bands in the region $200 < \lambda < 320$ nm. The first in the region $200 < \lambda < 250$ nm has four maxima at 209.0 nm ($\epsilon_{209} = 44354.3$), 220 nm ($\epsilon_{220} = 32670.1$), 230 nm ($\epsilon_{230} = 19903.4$) and 239 nm ($\epsilon_{239} = 9719.5$). The second in the region $260 < \lambda < 320$ nm has three maxima at 289.7 nm ($\epsilon_{289.7} = 25357.4$), 302.5 nm ($\epsilon_{302.5} = 21833.2$) and 314.2 nm ($\epsilon_{314.2} = 25011.9$) and inflexion at 278.0 nm ($\epsilon_{278.0} = 21833.3$). The wave lengths 220.0 and 302.5 nm differ only slightly from the dispersion constants appearing in the two term equations describing the optical rotation of acid 13.

Our studies on optical relationships in the homologous series of 9,9-methyl-alkyl-fluorene-2-carboxylic acids require the determination of principal chiroptical properties of other homologues. The material investigated until the present time makes it possible to state only that 9-propyl-fluorene-2-carboxylic acids [1] in all the solvents used in the investigations and in all the range of λ values have much higher molar rotations than 9,9-methyl-propyl-fluorene-2-carboxylic acids studied in the present work. This means that the introduction of the second alkyl (methyl) to the chirality center causes a considerable decrease of molar rotation. Further studies on these relationships will be continued.

EXPERIMENTAL

The m. p. are uncorrected. The IR and UV spectra were obtained by means of UNICAM SP-200 and SP-700 spectrophotometers, ORD spectra by means of Perkin-Elmer 241-MC polarimeter and JASCO (ORD/CD/UV/5) spectropolarimeter and CD curves by means of JASCO (ORD/CD/UV/5) spectropolarimeter. The compounds were analyzed in the form of suspension in paraffin oil (IR) and in the solutions described in the text.

1. 9,9-Methyl-propyl-fluorene 2

25 g (0.6 mole) of sodamide was introduced into a solution of 125 g (0.6 mole) of 9-propyl-fluorene (b. p. $171-172^\circ$) at 14 mm Hg, lit. [5] b. p. $170-172^\circ/14$ mm Hg) in 400 ccm of decalene. The suspension was stirred mechanically and was heated for 4 h on oil bath at 180° under a reflux condenser closed with a CaCl_2 tube. During this time a stream of dry nitrogen was passed through the suspension. The product (fine red crystals) was filtered and was washed with dry petroleum ether (2×100 ccm). It was dissolved in 1 litre of benzene and 180 g of CH_3I was added dropwise with stirring. The solution was refluxed for 5 h (CaCl_2 tube). NaI separated and was filtered off. The excess of CH_3I and

the solvent were distilled off. The residue was distilled under reduced pressure collecting the fraction boiling at 178–180°/14 mm Hg. The distillate soon solidified. The product (78 g) was crystallized from 96% ethanol (450 ccm). Needles m. p. 63–64°. Yield 50 g. The product is readily soluble in benzene, chloroform and acetone and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{17}H_{19}$ (222.31) – calculated: 91.81% C, 8.16% H;
found: 91.93% C, 8.03% H.

2. 9,9-Methyl-propyl-2-acetylfluorene (3)

110 g of 9,9-methyl-propyl-fluorene (2) was dissolved in 350 ccm of CS_2 . 130 g of $AlCl_3$ was added. The mixture was heated on water bath at 40° under reflux condenser closed with $CaCl_2$ tube and 51 ccm of acetic anhydride was added dropwise with stirring during 1 h. Then the mixture was heated at 40° for 30 min. and after cooling it was poured to a mixture of ice (1 kg) and 150 ccm of dilute (1:3 V/V) hydrochloric acid. The CS_2 layer was separated and after washing with water (2×150 ccm) it was dried with $MgSO_4$. The solvent was distilled off and the residue was distilled under reduced pressure collecting the fraction boiling at 217–221°/14 mm Hg. Light yellow oil. Yield 74 g. The ketone is readily soluble in the common organic solvents.

Analysis:

For the formula: $C_{19}H_{20}O$ (264.35) – calculated: 86.33% C, 7.28% H;
found: 86.14% C, 7.19% H.

3. Racemic 9,9-methyl-propyl-fluoreno-2-carboxylic acid (4)

84.1 g of ketone 3 was oxidized to the corresponding carboxylic acid according to ref. 1. The crude product (78 g) was crystallized from 96% ethanol (350 ccm). Needles m. p. 184–185°. Yield 50 g. The product is readily soluble in benzene and chloroform and fairly soluble in dioxane, methanol and 96% ethanol.

Analysis:

For the formula: $C_{18}H_{18}O_2$ (266.32) – calculated: 81.17% C, 6.81% H;
found: 80.96% C, 6.94% H.

IR (cm^{-1}): 750 $\delta C_{Ar}-H$ (subst. 1,2); 850, 915, 1150, $\delta C_{Ar}-H$ (subst. 1,2,4); 1000, 1025, 1125, 1225 $\delta C_{Ar}-H$ (subst. 1,2 and 1,2,4); 1470, 1495, 1590, 1615 $\nu C_{Ar}=C_{Ar}$; 940 δOH ; 1275, 1310, 1440 δOH and $\nu C-O$; 1680 $\nu C=O(COOH)$.

4. Amide of racemic 9,9-methyl-propyl-fluorene-2-carboxylic acid (5)

4 g of powdered acid 4 was added to 7 ccm of thionyl chloride and was refluxed on water bath ($CaCl_2$ tube) for 0.5 h. The excess of $SOCl_2$ was distilled off under reduced

pressure (12 mm Hg, water bath at 40°). The oily residue was treated with 50 ccm of 20% ammonia and was refluxed for 1 h on water bath. The product was filtered (2.4 g) and was crystallized from 50% ethanol (60 ccm). Needles m. p. 190–191°. Yield 1.1 g. The product is readily soluble in benzene, chloroform, methanol and 96% ethanol and is sparingly soluble in petroleum ether.

Analysis:

For the formula: $C_{18}H_{19}NO$ (265.34) – calculated: 5.28% N;
found: 5.29% N.

5. Methylamide of racemic 9,9-methyl-propyl-fluorene-2-carboxylic acid (6)

5.3 g of racemic acid 4 was converted into methylamide as in section 4, using 15 ccm of $SOCl_2$ and 140 ccm of 25% methylamine solution. The product (5 g) was crystallized from methanol (25 ccm). Plates m. p. 170–171°. Yield 3.9 g. It is readily soluble in benzene and chloroform, fairly soluble in methanol and 96% ethanol and sparingly soluble in petroleum ether.

Analysis:

For the formula: $C_{19}H_{21}NO$ (279.36) – calculated: 5.02% N;
found: 4.98% N.

6. Methylthioamide of racemic 9,9-methyl-propyl-fluorene-2-carboxylic acid (7)

1.39 g of methylamide 6 was converted into methylthioamide according to ref. 1, using 0.44 g of potassium polysulphide [6] and 0.47 g of phosphorus pentasulphide. The crude product (1.2 g) was crystallized from 75% ethanol (20 ccm). Light yellow needles m. p. 112–113°. Yield 0.57 g. The product is readily soluble in benzene, chloroform and acetone and is fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{19}H_{21}NS$ (295.43) – calculated: 4.74% N;
found: 4.98% N.

7. p-Bromophenacyl ester of racemic 9,9-methyl-propyl-fluorene-2-carboxylic acid (8)

2.6 g of racemic acid 4 was converted into its p-bromophenacyl ester as in ref. 7 using 2.8 g of p-bromophenacyl bromide and 85 ccm of methanol. The crude product (2.3 g) was crystallized from 96% ethanol (60 ccm). Needles m. p. 108°. Yield 2.4 g. The ester is readily soluble in benzene and chloroform and is sparingly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{26}H_{23}BrO_3$ (463.36) — calculated: 67.34% C, 5.00% H;
found: 67.22% C, 5.22% H.

8. p-Nitrobenzyl ester of racemic 9,9-methyl-propyl-fluorene-
-2-carboxylic acid (9)

2.6 g of racemic acid 4 was converted into its p-nitrobenzyl ester according to ref. 7 using 2.1 g of p-nitrobenzyl bromide and 125 ccm of methanol. The crude product was crystallized from 96% ethanol (70 ccm). Plates m. p. 116–117°. Yield 2 g. The product is readily soluble in benzene and chloroform and is sparingly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{25}H_{23}O_4N$ (401.44) — calculated: 3.48% N;
found: 3.58% N.

9. Cinchonidine salt of dextrorotatory 9,9-methyl-propyl-fluorene-
-2-carboxylic acid (10)

21.28 g (0.08 mole) of powdered acid 4 was mixed with 19.72 g (0.08 mole) of cinchonidine and was dissolved in 210 ccm of boiling 90% acetone. The solution was filtered when it was still hot and was allowed to stand at room temperature. After 14 h the first crop of crystals was filtered off. Needles m. p. 163–164°, $[\alpha]_D^{20} = -50.8^\circ$ ($c = 0.6, d = 2, \alpha = -0.61^\circ$) in methanol. After three crystallizations from 90% acetone the product had constant physical properties. Needles m. p. 169–170° with decompn., $[\alpha]_D^{20} = -47.5^\circ$ ($c = 0.6, d = 2, \alpha = -47.5^\circ$) in methanol. Yield 1.2 g. The salt is readily soluble in benzene, chloroform acetone, methanol and 96% ethanol and is insoluble in water.

Analysis:

For the formula: $C_{37}H_{40}N_2O_3$ (560.72) — calculated: 4.99% N;
found: 5.05% N.

10. Dextrorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (11)

1.2 g of cinchonidine salt 10 was converted into free acid according to ref. 1. The product (0.5 g) was crystallized from 80% ethanol (10 ccm). Fine needles m. p. 135–136° and $[\alpha]_D^{20} = +35.0^\circ$ ($c = 0.6, d = 2, \alpha = +0.42^\circ$) in methanol. Yield 0.4. The product is readily soluble in acetone, methanol and 96% ethanol and is insoluble in water.

Analysis:

For the formula: $C_{18}H_{18}O_2$ (266.32) — calculated: 81.17% C, 6.81% H;
found: 81.24% C, 7.03% H.

Tab. 2. Fractional crystallization of cinchonidine salt of 9,9-methyl-propyl-fluorene-2-carboxylic acid (crystallization time 24 h.)

Fraction No.	Amount of 90% acetone (ccm)	Amount of salt (g)	Specific rotation in methanol $[\alpha]_D^{20}$	M. p. of the salt with decompn. °C
1.	210	7.0	-50.8	163-164
1.1.	80	4.0	-49.2	167-169
1.1.1.	70	2.0	-48.0	168-170
1.1.1.1.	60	1.2	-47.5	169-170

11. Brucine salt of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (12)

18.64 (0.07 mole) of powdered acid 4 was mixed with 27.61 g (0.07 mole) of brucine and was dissolved in 100 ccm of boiling 75% ethanol. The solution was filtered when it was still hot and was allowed to stand at room temperature. After 20 h the first crop of crystals was filtered off. Needles (19 g) m. p. 104-106° with decompn., $[\alpha]_D^{20} = -24.2^\circ$ ($c = 0.6$, $d = 2$, $\alpha = -0.29^\circ$) in methanol. The first fraction of the salt (19.0 g) was crystallized from 75% ethanol (170 ccm, crystallization time 20 h). The resulting homogeneous product (14.0 g) had constant physical properties. Needles m. p. 104-106° with decompn., $[\alpha]_D^{20} = -25.8^\circ$ ($c = 0.6$, $d = 2$, $\alpha = -0.31^\circ$) in methanol. Yield 14 g. The salt is readily soluble in chloroform, acetone, methanol and 96% ethanol and is insoluble in water.

Analysis:

For the formula: $C_{41}H_{44}O_6N_2$ (674.82) - calculated: 4.23% N;
found: 4.28% N.

12. Laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (13)

14 g of brucine salt 12 was converted into the free acid according to ref. 1. The product (5 g) was crystallized from 96% ethanol (25 ccm). Colorless needles n. p. 137°, $[\alpha]_D^{20} = -35.2^\circ$ ($c = 0.6$, $d = 2$, $\alpha = -0.43^\circ$) in methanol. Yield 4 g. The compound is readily soluble in benzene, chloroform, methanol and 96% ethanol and is insoluble in water.

Analysis:

For the formula: $C_{18}H_{18}O_2$ (266.32) - calculated: 81.17% C, 6.81% H;
found: 80.96% C, 6.71% H.

IR (cm^{-1}): 750 $\delta C_{Ar}-H$ (subst. 1,2); 840, 910, 1150 $\delta C_{Ar}-H$ (subst. 1,2,4); 1005, 1015, 1120, 1220 $\delta C_{Ar}-H$ (subst. 1,2 and 1,2,4); 1470, 1495, 1585, 1610 $\nu C_{Ar}=C_{Ar}$; 945 δOH ; 1270, 1300, 1430 δOH and $\nu C-O$; 1680 $\nu CO(COOH)$.

UV: $\lambda = 209.0$ nm ($\epsilon_{209.0} = 44354.3$), 220 nm ($\epsilon_{220} = 32670.1$), 230 nm ($\epsilon_{230} = 19903.4$), 239 nm ($\epsilon_{239} = 9719.5$), 278 nm ($\epsilon_{278} = 27833.3$), 289.7 nm ($\epsilon_{289.7} = 25357.4$), 302.5 nm ($\epsilon_{302.5} = 21833.2$) 314,2 nm ($\epsilon_{314.2} = 25011.9$).

13. Amide of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (14)

2 g of acid 13 was converted into its amide as in section 4. The product (1.9 g) was crystallized from 58 ccm of ethanol (30 ccm). Needles m. p. 173°, $[\alpha]_D^{20} = -36.3^\circ$ ($c = 0.8$, $d = 2$, $\alpha = -0.58^\circ$) in methylethylketone. Yield 1.3 g. The compound is readily soluble in benzene, chloroform, methanol, 96% ethanol, and is insoluble in water.

Analysis:

For the formula: $C_{18}H_{19}NO$ (265.20) – calculated: 5.28% N;
found: 5.32% N.

14. Methylamide of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (15)

5.3 g of acid 13 was converted into methylamide as in section 5. The crude product (5.2 g) was crystallized from methanol (20 ccm). Plates m. p. 160°, $[\alpha]_D^{20} = -41.0^\circ$ ($c = 0.5$, $d = 2$, $\alpha = -0.41^\circ$) in methanol. Yield 2.4 g. The compound is readily soluble in benzene and chloroform, fairly soluble in methanol and 96% ethanol, sparingly soluble in petroleum ether, and insoluble in water.

Analysis:

For the formula: $C_{19}H_{21}NO$ (279.36) – calculated: 5.02% N;
found: 5.21% N.

15. Methylthioamide of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (16)

2.09 g of methylamide 15 was converted into methylthioamide as in section 6. using 0.66 g of potassium polysulphide [6], 0.70 g of phosphorus pentasulphide and 17 ccm of xylene. The crude product (1.7 g) was crystallized from 96% ethanol (20 ccm). Yellow rods m. p. 139°, $[\alpha]_D^{20} = -83.3^\circ$ ($c = 0.6$, $d = 2$, $\alpha = -1.0^\circ$) in methanol. Yield 0.9 g. The compound is readily soluble in benzene and chloroform, fairly soluble in methanol and 96% ethanol, sparingly soluble in petroleum ether and insoluble in water.

Analysis:

For the formula: $C_{19}H_{21}NS$ (295.43) – calculated: 4.74% N;
found: 4.84% N.

UV spectrum: $\lambda = 214$ nm ($\epsilon_{214} = 21674.8$); 253 nm ($\epsilon_{253} = 5692.4$); 290 nm ($\epsilon_{290} =$

= 19704.4); 300 nm ($\epsilon_{300} = 19047.6$); 313 nm ($\epsilon_{313} = 21018.0$); 335 nm ($\epsilon_{335} = 8757.5$); 353 nm ($\epsilon_{353} = 3065.1$).

16. p-Bromophenacyl ester of laevorotatory 9,9-methyl-propyl-fluorene-2-carboxylic acid (17)

2 g of acid 13 was converted into its p-bromophenacyl ester as in section 7 using 2.1 g of p-bromophenacyl bromide and 120 ccm of methanol. The crude product (2.2 g) was crystallized from methanol (70 ccm). Needles m. p. 113° , $[\alpha]_D^{20} = -24.4^\circ$ ($c = 0.8$, $d = 2$, $\alpha = -0.39^\circ$) in methylethylketone. Yield 1.2 g. The ester is readily soluble in benzene and chloroform, fairly soluble in methanol and 96% ethanol.

Analysis:

For the formula: $C_{26}H_{23}BrO_3$ (463.36) – calculated: 67.39% C, 5.00% H;
found: 67.32% C, 5.15% H.

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STRESZCZENIE

Opisano syntezę i podstawowe właściwości rac. kwasu 9,9-metylo-propylo-fluoreno-2-karboksylowego. Kwas racemiczny rozszczepiono w drodze krystalizacji frakcyjnej diastereomerycznych soli z optycznie czynnymi zasadami na enancjomery. Określono w obszarze $350 < \lambda < 600$ nm dyspersję rotacji optycznej lewoskrętnego enancjomeru, jego amidów i estrów. Na podstawie badania widm ORD i CD przypisano poszczególnym antymerom względne konfiguracje przestrzenne. Wyznaczono dwuczłonowe równania opisujące rotację optyczną lewoskrętnego enancjomeru i jego amidu w kilku rozpuszczalnikach w badanym zakresie widmowym. Wykazano zgodność wartości numerycznych stałych dyspersyjnych występujących w dwuczłonowych równaniach określających rotację optyczną enancjomerycznych kwasów 9,9-metylo-propylo-fluoreno-2-karboksylowych z długościami fal optycznie czynnych pasm w nadfioletowej części widma.

РЕЗЮМЕ

В данной работе представлен синтез и основные свойства рацемической 9,9-метило-пропило-флюорено-2-карбоксовой кислоты. Рацемическую кислоту расщеплено путем фракционной кристаллизации диастереомерических солей с оптически деятельными основаниями на энантиомары. В области $350 < \lambda <$

600 nm определено дисперсию оптического вращения левовращающего энантиомера, его амидов и сложных эфиров. На основе исследования ORD и CD спектров отдельным антимером приписано относительные пространственные конфигурации. Представлено двучленные уравнения представляющие оптическое вращение левовращающего энантиомера и его амида в нескольких растворителях в исследованный спектрный период. Представлено совпадение численных постоянных дисперсионных величин выступающих в двучленных уравнениях определяющих оптическое вращение энантиомерических 9,9-метило-пропило-флюрено-2-карбоксилых кислот с длинами волн оптически деятельных полос в ультрафиолетовой части спектра.