

Institut Chemil UMCS
Pracownia Naukowo-Badawcza Stereo- i Spektrochemii
Kierownik: Prof. dr Marian Janczewski

Marian JANCZEWSKI, Ewa PAWŁOWSKA

Effect of Molecular Structure on Optical Properties of Systems Containing Carbon Chirality Centres. Part XXVII. 9-Butyl-9-methylfluorene-2-carboxylic Acids and Some of Their Derivatives

Wpływ budowy cząsteczkowej na własności optyczne układów z węglowymi centrami chiralności. Część XXVII. Kwasy 9-butylo-9-metylo-fluoreno-2-karboksylowe i niektóre ich pochodne

Влияние молекулярного строения на оптические свойства систем с углеродными центрами хиральности. XXVII. 9-бутил-9-метил-флюорендикарбоксильные кислоты и некоторые их производные

Optical rules in homologous series of systems containing carbon chirality centres with restricted rotation were studied in our laboratory at first on the example of 9-alkylfluorene-2-carboxylic acids [1, 2]. Easy occurring racemization processes necessitated the reconstruction of chirality centre on the way of mobile hydrogen substitution for the methyl group, i.e. using 9-alkyl-9-methylfluorene-2-carboxylic acids in our experiments.

So far, only two optically active systems: 9-ethyl-[4] and 9-propyl-9-methylfluorene-2-carboxylic acids have been studied in this group of compounds. The chirooptical studies carried out permitted to find that: (I) compounds rotating the plane of polarized light in the visible part of the spectrum in the same direction have the same configuration; (II) the dependence of the molar rotation of the free acids

* Part XXVI: M. Janczewski, R. Kutyła, Ann. Univ. Mariae Curie-Skłodowska, Lublin, in press.

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

in the visible and the ultraviolet parts of the spectrum on the wavelength can be described by two-term equations of the type $\sum \frac{A_m}{\lambda^2 - \lambda_m^2}$; (III) in the region $480 < \lambda < 623$ nm the functions $\frac{1}{\alpha}(\lambda^2)$ are approximately linear; (IV) in the same region the homologous 9-alkylfluorene-2-carboxylic acids in the solvents used in the measurements show an increase in molar rotation accompanying the increase of the size of the aliphatic substituent in position 9 of the fluorene ring. In order to obtain a larger experimental material for our further studies we have prepared and examined compounds belonging to higher homologues of 9-ethyl-9-methylfluorene-2-carboxylic acid.

In the present communication we have described the preparation of racemic 9-butyl-9-methylfluorene-2-carboxylic acid, its resolution and principal chiroptical properties of the laevorotary enantiomer and its esters and amides.

The starting material was 9-butyl-9-methylfluorene (2), which was obtained by the reaction of the sodio derivative of 9-butylfluorene (1) with methyl iodide. Product 2 was acetylated giving 9-butyl-9-methyl-2-acetylfluorene. The structure of acetyl derivatives of 9,9-dialkylfluorenes was found previously in our laboratory [4]. The non-described racemic 9-butyl-9-methylfluorene-2-carboxylic acid 4 was prepared by oxidation of ketone 3 with sodium hypobromite in dilute dioxane. The structure of 4 was confirmed by the elemental analysis and IR spectra. Acid 4 yielded readily crystallizing amides 5, 6 and 7 and esters 8 and 9.

Acid 4 was resolved by fractional crystallization of its salts with brucine and cinchonidine. The equimolar salt of acid 4 with brucine yielded a salt of the laevorotary acid 11 which had m.p. 99-100° (decomp.) and $[\alpha]_D^{20} = -33,3^\circ$ (methanol). The equimolar salt of acid 4 with cynchonidine afforded a salt of dextrorotary enantiomer (13) m.p. 157-158° (decomp.) and $[\alpha]_D^{20} = -39,2^\circ$ (methanol).

Optically active 9-butyl-9-methylfluorene-2-carboxylic acids 11 and 13 freed in the usual way from the alkaloids and purified by crystallization from dilute ethanol had relatively high specific rotations $[\alpha]_D^{20} = -51,2^\circ$ and $+49,8^\circ$ (methanol). It should be mentioned that the enantiomeric 9-butyl-9-methylfluorene-2-carboxylic acids are very resistant to racemization.

An equimolar mixture of the enantiomers after crystallization produced racemic acid 4. The m.p. of the racemate was slightly

higher ($\Delta t = 33^\circ$) than that of the antipodes. The infrared spectrum of racemic acid 4 was considerably different in the "finger print" region from the identical spectra of enantiomers 11 and 13. The relatively difficult resolution of acid 4 and the physical properties quoted above indicate that racemic acid 4 belongs to the type of true racemate.

In order to obtain an ampler comparative material for chirooptical studies we have prepared the following derivatives of laevorotatory acid 11: amide 14, methylamide 15, methylthioamide 16, and p-bromophenacyl ester 17. Molar rotations of laevorotatory acid 11, its amide 14 and p-bromophenacyl ester 17 are shown in Tab. 1.

A comparison of the numerical values shows that the character of the solvent has only a slight effect on the molar rotation. The analysis of the data collected in the table indicates that the optical rotatory dispersion of the examined compounds in the visible part of the spectrum has the character of normal dispersion.

In the previous communication we showed that the homologous 9-propyl[5]- and 9-ethyl[4]-9-methylfluorene-2-carboxylic acids and 9-methylfluorene-2-carboxylic acids [1], having the same directions of rotations in the visible part of the spectrum, had the same spatial structures. Methylthioamide of laevorotatory 9-methylfluorene-2-carboxylic acid was employed as a reference system in our comparative configurational studies. In order to find if optically active 9-butyl-9-methylfluorene-2-carboxylic acids (11, 13) reveal the same regularities, we tried to determine their Spatial structures.

It should be mentioned that the classical methods were found to be unsuitable for the configurational studies in view of small and often solvent-dependent optical shifts of the same derivatives of the acids examined, and because of the lack of tendency to form true racemates. For this reason we have solved this problem by analyzing ORD and CD curves of methylthioamides of laevorotatory 9-methylfluorene-2-carboxylic and 9-butyl-9-methylfluorene-2-carboxylic (11) acids. The ORD and CD curves of the mentioned methylthioamides of laevorotatory acid have (in methanol) analogous structures. The ORD curve of methylthioamide of laevorotatory 9-methylfluorene-2-carboxylic acid has a trough at $\lambda = 410$ nm, where $[\text{M}]_{410}^{20} = -1344_{20}^3$ (this curve intersects

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

Compound	Solvent	Concentration g/100ml	Molar		
			$\lambda=600$ nm	$\lambda=589$ nm	$\lambda=560$ nm
Laevorotatory 9-butyl-9-methyl- fluorene-2-carbo- xylic acid	E	0,40	134,6 (125,8)	138,8 (131,8)	151,4 (150,1)
	Ch	0,20	120,5 (120,2)	126,1 (126,3)	148,6 (144,9)
	THF	0,20	103,7 (104,2)	109,3 (109,2)	123,4 (124,5)
	DMF	0,219	120,3 (119,6)	122,9 (125,4)	143,4 (142,7)
Amide of laevo- rotatory 9-butyl- -9-methyl-fluorene- -2-carboxylic acid	E	0,198	163,6 (160,9)	169,3 (168,6)	191,9 (191,8)
	Ch	0,199	120,7 (117,6)	123,5 (123,3)	140,4 (140,7)
	THF	0,202	121,7 (121,4)	129,9 (127,2)	143,8 (144,9)
	DMF	0,202	138,3 (135,7)	141,1 (142,0)	160,4 (161,4)
p-Bromophenacyl ester of laevo- rotatory 9-butyl- -9-methyl-fluorene- -2-carboxylic acid	E	0,109	157,7	166,4	183,9
	Ch	0,200	148,0	152,8	181,4
	THF	0,200	138,4	148,0	176,6
	DMF	0,220	143,2	160,6	186,6

E = ethanol,

Ch = chloroform,

THF = tetrahydrofuran,

DMF = dimethylformamide.

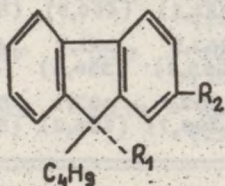
-fluorene-2-carboxylic acid and some of its derivatives

rotation

$\lambda=520$ nm	$\lambda=480$ nm	$\lambda=450$ nm	$\lambda=435$ nm	$\lambda=400$ nm	$\lambda=380$ nm	$\lambda=360$ nm	$\lambda=340$ nm
179,4 (183,3)	228,5 (230,6)	278,9 (281,9)	312,6 (315,5)	428,9 (430,2)	536,9 (537,2)	710,7 (710,4)	1047,1 (1049,2)
182,2 (178,9)	229,9 (228,9)	283,2 (284,2)	319,6 (321,1)	444,4 (449,5)	563,5 (571,5)	768,2 (769,5)	-
151,4 (152,2)	193,4 (191,9)	235,5 (234,9)	263,5 (263,2)	361,7 (359,8)	447,2 (449,7)	594,3 (594,4)	871,9 (871,7)
171,5 (174,0)	217,6 (218,8)	266,3 (267,0)	302,1 (298,7)	407,1 (406,2)	506,9 (509,0)	663,1 (667,0)	980,5 (980,1)
234,2 (233,5)	290,6 (292,7)	358,3 (356,2)	397,8 (397,5)	536,1 (535,8)	660,2 (661,4)	854,9 (857,7)	1216,1 (1217,4)
168,4 (172,3)	213,4 (217,6)	269,5 (266,9)	300,4 (299,2)	412,7 (409,3)	516,6 (511,3)	673,8 (673,4)	971,3 (974,9)
177,0 (176,8)	221,3 (222,4)	268,3 (271,4)	304,2 (303,3)	414,9 (410,9)	511,7 (509,0)	658,3 (662,3)	940,9 (940,8)
196,4 (196,1)	243,4 (245,2)	298,7 (297,5)	331,9 (331,4)	445,3 (444,6)	550,4 (547,0)	705,3 (707,3)	1004,0 (1005,0)
227,8	289,1	359,1	402,9	551,9	700,7	963,5	1462,8
229,1	286,4	350,9	400,9	558,5	716,1	988,2	1355,8
219,6	276,9	338,9	381,9	525,1	668,3	883,2	1336,4
225,7	286,4	351,5	394,9	546,8	690,0	954,8	-

the λ axis at $\lambda = 367$ nm), whereas the CD curve has a negative maximum at $\lambda = 356$ nm, where $[\theta]_{365}^{20} = -710.4$. Analogously, the ORD curve of methylthioamide of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (11) has a trough at $\lambda = 405$ nm, where

Fig. 1.



- 1: $R_1 = H, R_2 = H$
2: $R_1 = CH_3, R_2 = H$
3: $R_1 = CH_3, R_2 = COCH_3$
4: $R_1 = CH_3, R_2 = COOH$
5: $R_1 = CH_3, R_2 = CONH_2$
6: $R_1 = CH_3, R_2 = CO \cdot NH \cdot CH_3$
7: $R_1 = CH_3, R_2 = CS \cdot NH \cdot CH_3$
8: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot C_6H_4 \cdot NO_2$
9: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4 \cdot Br$
10: $R_1 = CH_3, R_2 = COOH \cdot Bruc.$
11: $R_1 = CH_3, R_2 = COOH (-)$
12: $R_1 = CH_3, R_2 = COOH \cdot Cynch.$
13: $R_1 = CH_3, R_2 = COOH (+)$
14: $R_1 = CH_3, R_2 = CO \cdot NH_2 (-)$
15: $R_1 = CH_3, R_2 = CONHCH_3 (-)$
16: $R_1 = CH_3, R_2 = CS \cdot NH \cdot CH_3 (-)$
17: $R_1 = CH_3, R_2 = CO \cdot OCH_2 \cdot CO \cdot C_6H_4 \cdot Br (-)$

Bruc. = brucine

Cynch. = cinchonidine

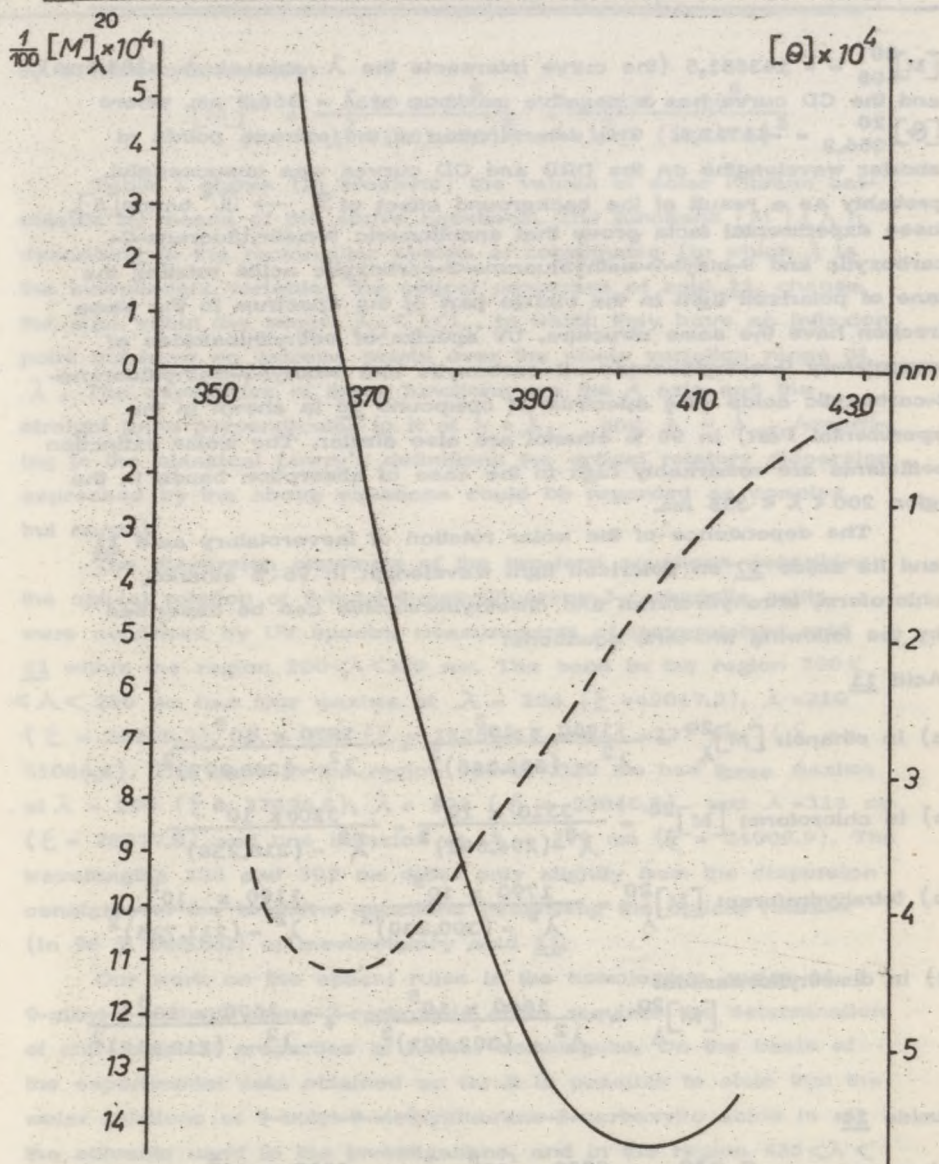


Fig. 2. Optical rotatory dispersion (ORD —) and circular dichroism (CD - - -) curves of methylthioamide of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid in 96 % ethanol (the measurements were carried out in JASCO ORD/CD/UV/5 spectropolarimeter). ORD: ($C=0,00125 \text{ g}/100 \text{ cm}^3$, $d=0,05 \text{ dm}$), $[M]_{366}^{20} = -443588,5$, $\alpha = -0,029^\circ$; $[M]_{366}^{20} = 0$, $\alpha = 0$; CD: ($c=0,0004039 \text{ mol}/\text{dm}^3$, $d=0,5 \text{ cm}$), $[\theta]_{366}^{20} = -44762,4$, $A = 0,00274$.

$[M]_{405}^{20} = -143581,5$ (the curve intersects the λ axis at $\lambda = 386,6\text{nm}$), and the CD curve has a negative maximum at $\lambda = 366,2\text{ nm}$, where $[\Theta]_{366,2}^{20} = -44762,4$. The determination of the extreme points at shorter wavelengths on the ORD and CD curves was unsuccessful, probably as a result of the background effect of $\mathcal{J} \rightarrow \mathcal{J}^*$ bands [6]. These experimental facts prove that enantiomeric 9-methylfluorene-2-carboxylic and 9-butyl-9-methylfluorene-2-carboxylic acids rotating the plane of polarized light in the visible part of the spectrum in the same direction have the same structure. UV spectra of methylthioamides of laevorotatory 9-methylfluorene-2-carboxylic and 9-butyl-9-methylfluorene-2-carboxylic acids (the spectrum of compound 16 is shown in the Experimental Part) in 96 % ethanol are also similar. The molar extinction coefficients are remarkably high in the case of absorption bands in the region $200 < \lambda < 335\text{ nm}$.

The dependence of the molar rotation of laevorotatory acid 11 and its amide 17 on polarized light wavelength in 96 % ethanol, chloroform, tetrahydrofuran and dimethylformamide can be described by the following two-term equations:

Acid 11

$$\text{a) in ethanol: } [M]_{\lambda}^{20} = \frac{1960 \times 10^5}{\lambda^2 - (302,645)^2} + \frac{1670 \times 10^5}{\lambda^2 - (209,877)^2}$$

$$\text{b) in chloroform: } [M]_{\lambda}^{20} = \frac{3310 \times 10^5}{\lambda^2 - (294,562)^2} - \frac{3200 \times 10^5}{\lambda^2 - (218,238)^2}$$

$$\text{c) tetrahydrofuran: } [M]_{\lambda}^{20} = \frac{1790 \times 10^5}{\lambda^2 - (300,230)^2} + \frac{1190 \times 10^5}{\lambda^2 - (211,725)^2}$$

d) in dimethylformamide:

$$[M]_{\lambda}^{20} = \frac{1800 \times 10^5}{\lambda^2 - (302,591)^2} + \frac{1670 \times 10^5}{\lambda^2 - (210,112)^2}$$

Amide 14

$$\text{a) in ethanol: } [M]_{\lambda}^{20} = \frac{2330 \times 10^5}{\lambda^2 - (298,295)^2} + \frac{2350 \times 10^5}{\lambda^2 - (216,572)^2}$$

$$\text{b) in chloroform: } [M]_{\lambda}^{20} = \frac{2220 \times 10^5}{\lambda^2 - (296,864)^2} + \frac{1120 \times 10^5}{\lambda^2 - (220,212)^2}$$

$$\text{c) in tetrahydrofuran: } [M]_{\lambda}^{20} = \frac{2000 \times 10^5}{\lambda^2 - (296,132)^2} + \frac{1490 \times 10^5}{\lambda^2 - (220,723)^2}$$

d) in dimethylformamide:

$$[M]_{\lambda}^{20} = \frac{1650 \times 10^5}{\lambda^2 - (301.360)^2} + \frac{2330 \times 10^5}{\lambda^2 - (216.905)^2}$$

Table 1 shows (in brackets) the values of molar rotation calculated by means of the above equations. The functions $[M](\lambda)$, describing in the rectangular system of coordinates (in which λ is the independent variable) the optical properties of acid 11, change the sign within the range $\lambda_2 < \lambda < \lambda_1$, in which they have an inflexion point but have no extreme points over the whole variation range of λ . The asymptotes of these functions are the λ axis and the straight lines perpendicular to it at $\lambda = \lambda_1$ and $\lambda = \lambda_2$. According to the classical Lowry's definitions the optical rotatory dispersion expressed by the above equations could be regarded as complex but normal.

The dispersion constants of the two-term equations describing the optical rotation of 9-butyl-9-methylfluorene-2-carboxylic acids were confirmed by UV spectra measurements of laevorotatory acid 11 within the region $200 < \lambda < 320$ nm. The band in the region $200 < \lambda < 250$ nm has four maxima at $\lambda = 208$ ($\epsilon = 49047,2$), $\lambda = 210$ ($\epsilon = 36240,3$), $\lambda = 229$ ($\epsilon = 15559,6$) and $\lambda = 237$ nm ($\epsilon = 11085,4$). The band in the region $250 < \lambda < 320$ nm has three maxima at $\lambda = 290$ ($\epsilon = 27896,8$), $\lambda = 302$ ($\epsilon = 23040,2$) and $\lambda = 314$ nm ($\epsilon = 28277,9$) and one inflexion at $\lambda = 279$ nm ($\epsilon = 24008,9$). The wavelengths 208 and 302 nm differ only slightly from the dispersion constants of the two-term equations describing the optical rotation (in 96 % ethanol) of laevorotatory acid 11.

Our work on the optical rules in the homologous series of 9-alkyl-9-methylfluorene-2-carboxylic acids requires the determination of chiroptical properties of further homologues. On the basis of the experimental data obtained so far it is possible to state that the molar rotations of 9-butyl-9-methylfluorene-2-carboxylic acids in all the solvents used in the investigations, and in the region $435 < \lambda < 600$ nm are considerably higher ($\% \Delta R = 46,16$ %) than those of 9-propyl-9-methylfluorene carboxylic acids studied previously. Thus, the substitution of butyl for propyl radical on the chirality centre caused a considerable increase in the molar rotation of the system. Although our observations do not contradict the classical Tschugaev's rules, it should be stressed that the functions $[M]_{\lambda}^t(M)$

corresponding to the systems examined in the classical Tschugaev's studies and to the dialkylfluorenes studies by us do not show the close similarity expected. The studies on these phenomena will be continued.

E X P E R I M E N T A L

The melting points are uncorrected, IR and UV spectra were measured by means of Unicam SP-200 and SP-700 spectrophotometers. ORD measurements were carried out in Perkin-Elmer 241-MC polarimeter and CD Jasco /ORD/CD/UV/V spectropolarimeter. The compounds were analysed in the form of suspensions in paraffin oil (IR) and in solutions specified in the text.

1. 9-Butylfluorene (1)

A mixture of 83.0 g of fluorene, 200 ml of n-butanol and 10 ml of 80 % NaOH was heated in an autoclave to 200-220°C with stirring for 20 h. Then the reaction solution was neutralized to pH 7 with diluted (1:1 V/V) hydrochloric acid, washed with water and dried with anhydrous MgSO₄. Butanol was distilled off under reduced pressure, collecting the fraction boiling at 198-199°C/20mm Hg [9]. The product was colourless oil readily soluble in organic solvents; yield 80 g.

2. 9-Butyl-9-methylfluorene (2)

9-Butylfluorene (1) (111g) was dissolved in 450 ml of decalin and 21.25 g of NaNH₂ was added. The mixture was vigorously stirred and refluxed (CaCl₂ tube) on oil bath (bath temperature 180°) for 4 h. During this time a stream of dry nitrogen was passed through the reacting mixture. The crude product (sodioderivative) was filtered off, washed with petroleum ether, suspended in 1.2 dm³ of benzene. Methyl iodide was added dropwise and the mixture was refluxed (CaCl₂ tube) with stirring on water bath during 5 h. NaI was filtered off and the residue, after removal of the excess CH₃I and benzene, was distilled under reduced pressure, collecting the fraction boiling at 171-176°C/12 mm Hg. The product was colourless oil; yield 80 g.

Analysis: For C₁₈H₂₀ (236.34) - Calcd: 91,5 % C, 8,6 % H;
found: 91,4 % C, 8,6 % H

3. 2-Acetyl-9-butyl-9-methylfluorene (3)

9-Butyl-9-methylfluorene (2) (118,17 g) was dissolved in 350 ccm of CS_2 and 133,34 g of anhydrous $AlCl_3$ was added. The mixture was vigorously stirred and refluxed on a water bath ($CaCl_2$ tube, bath temperature $40^\circ C$) and was treated dropwise for 1 h with 51 ccm of acetic anhydride. Then it was heated for further 30 min and after cooling it was poured into a mixture of ice (500 g) and dilute (1:1) hydrochloric acid (150 ccm). When the ice dissolved, the solution of the ketone in CS_2 was separated and, after washing with water (3x150 ccm), it was dried with anhydrous $MgSO_4$. The solvent was distilled off and the residue was distilled under reduced pressure, collecting the fraction boiling at $217-220^\circ C/12$ mm Hg. Almost colourless oil; yield 90 g.

4. Racemic 9-butyl-9-methylfluorene-2-carboxylic acid (4)

Ketone 3 (69,6 g) was oxidized to corresponding carboxylic acid according to ref [1]. The crude product (70 g) was crystallized from methanol (300 ml). Needles, m.p. $51-62^\circ C$.

Analysis: For $C_{19}H_{20}O_2$ (280,5) - Calcd.: 81,4 % C; 7,2 % H; found: 81,2 % C, 7,3 % H.

IR (cm^{-1}): 760, $\delta C_{Ar}-H$ (subst. 1,2); 860, 910, 1150 $\delta C_{Ar}-H$ (subst. 1, 2, 4); 1000, 1020, 1120, 1220 $\delta C_{Ar}-H$ (subst. 1, 2 and 1,2,4); 1430, 1495, 1580, 1610 ($\nu C_{Ar} = C_{Ar}$); 940 ($\delta OH, COOH$); 1270, 1300, 1420 (δOH and $\nu C-O(COOH)$); 1680 ($\nu C = O(COOH)$).

5. Amide of racemic 9-butyl-9-methylfluorene-2-carboxylic acid (5)

Acid 4 (4,2 g) was converted into its amide according to ref [4]. The crude product (3,6 g) was crystallized from methanol (30 ccm). Needles, m.p. $166-167^\circ C$; yield 1,3 g.

Analysis: For $C_{19}H_{21}NO$ (274,36) - Calcd: 5,0 % N; found: 5,2 % N.

6. Methanamide of racemic 9-butyl-9-methylfluorene-2-carboxylic acid (6)

Racemic acid 4 (5,6 g) was converted into its methanamide under conditions described in ref [4], using 15 of $SOCl_2$ and 200 ccm of 25 % methylamine. The product (5,2 g), was crystallized

from diluted (3:1-V/V) ethanol (75 ml). Needles, m.p. 193°C; yield 2.4 g.

Analysis: For $C_{20}H_{23}NO$ (293,34) - Calcd: 4,8 % N; found: 4,9 % N.

7. Methylthioamide of racemic 9-butyl-9-methylfluorene-2-carboxylic acid (7)

Methylamide 6 (2,13 g) was converted into corresponding thioamide as in ref. [1], using 0,88 g of potassium polysulfide [8] and 0,94 of phosphorus pentasulfide. The crude product (1,8 g) was crystallized from 96 % ethanol (50 ml). Pale yellow needles, m.p. 167-168°C; yield 0,5 g.

Analysis: For $C_{20}H_{23}NS$ (309,46) - Calcd: 4,5 % N; found: 4,7 % N.

8. p-Nitrobenzyl ester of racemic 9-butyl-9-methylfluorene-2-carboxylic acid (8)

Acid 4 was converted into its p-nitrobenzyl ester according to ref. [2], using 2,1 g of p-nitrobenzyl bromide. Esterification was carried out in 96 % ethanol (120 ml). The crude product (2,6 g) was crystallized from 96 % ethanol (70 ml). Rods, m.p. 93°C; yield 0,9 g.

Analysis: For $C_{26}H_{25}NO_4$ (417,48) - Calcd: 3,4 % N; found 3,6 % N.

9. p-Bromophenacyl ester of racemic 9-butyl-9-methylfluorene-2-carboxylic acid (9)

Acid 4 (2,8 g) was converted into its p-bromophenacyl ester as in ref. [2], using 2,8 g of p-bromophenacyl bromide. Esterification was carried out in 94 % methanol (160 ml). The crude product (2,2 g) was crystallized from methanol (110 ml). Needles, m.p. 116-117°C, yield 1,2 g.

Analysis: For $C_{27}H_{25}BrO_3$ (477,38) - Calcd: 67,9 % C, 5,3 % H; found 67,8 % C; 5,3 % H.

10. Brucine salt of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (10)

Powdered acid 4 (19,82 g, 0,07 mole) was mixed with 27,6 g (0,07 mole) of brucine, and the mixture was dissolved in 60 ccm of boiling 65 % ethanol. The solution was allowed to stand at room temperature. After 24 h the first fraction of the salt was filtered off.

Needles (23 g), m.p. 97-101°C (decomp.), $[(\alpha)_D^{20}] = -23,3^\circ$

($c=0.6$, $d=2$, $\alpha = -0.30^\circ$ in methanol). The first fraction of the salt (23 g) was twice crystallized from 57.6 % methanol (crystallization time 24 h). The product (11.5 g) had physical properties which remained unchanged by further crystallization. Needles, m.p. $99-101^\circ\text{C}$ (decomp.) ($[\alpha]_D^{20} = -33.33^\circ$ ($c=0.6$, $d=2$, $\alpha = -0.40^\circ$, methanol).

Analysis: For $\text{C}_{42}\text{H}_{46}\text{N}_2\text{O}_6$ (674.82) - Calcd: 4.2 % N; found: 4.2 % N.

11. Levorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (11)

Brucine salt 10 (11.5 g) (m.p. $99-101^\circ\text{C}$, decomp., $(\alpha)_D^{20} = -33.33^\circ$) was converted into free acid according to ref [1]. The product (4 g) was crystallized from 70 % ethanol (25 ccm). Needles, m.p. $147-148^\circ\text{C}$, $[\alpha]_D^{20} = -51.25^\circ$ ($c=0.4$, $d=2$, $\alpha = -0.41^\circ$, methanol).

Analysis: For $\text{C}_{19}\text{H}_{20}\text{O}_2$ (280.35) - Calcd: 81.4 % C, 7.1 % H; found: 81.2 % C, 6.9 % H.

UV/ $\text{CHCl}_3/\lambda_{\text{max}}$: 210 ($\epsilon = 4691.6$), 231 ($\epsilon = 7272.8$), 281 ($\epsilon = 16623.5$), 292 ($\epsilon = 20996.6$), 306 ($\epsilon = 18642.8$), 316 ($\epsilon = 23917.9$) nm;

UV/ $\text{EtOH}/\lambda_{\text{max}}$: 208 ($\epsilon = 49047.2$), 218 ($\epsilon = 36240.9$), 229 ($\epsilon = 15559.6$), 237 ($\epsilon = 11085.4$), 279 ($\epsilon = 24008.9$), 290 ($\epsilon = 27896.2$), 302 ($\epsilon = 23040.2$), 314 ($\epsilon = 28277.9$) nm.

IR (cm^{-1}): 760 ($\delta \text{C}_{\text{Ar}}-\text{H}$) subst. 1,2); 850, 910, 1155 ($\delta \text{C}_{\text{Ar}}-\text{H}$) subst. 1,2,4); 1005, 1030, 1120, 1220 ($\delta \text{C}_{\text{Ar}}-\text{H}$) subst. 1,2 and 1,2,4); 1435, 1500, 1590, 1620 ($\nu \text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}$); 940 ($\delta \text{OH}(\text{COOH})$); 1270, 1310, 1420 (δOH , $\nu \text{C}=\text{O}(\text{COOH})$); 1680 ($\nu \text{C}=\text{O}(\text{COOH})$).

12. Cinchonidine salt of dextrorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (12)

The ethanolic filtrate remaining after filtration of the first fraction of brucine salt was evaporated under reduced pressure (12 mm Hg, water bath) to dryness. The resulting oily brucine salt was converted into free acid under conditions described in section 11. Needles (8.5 g), m.p. $164-166^\circ\text{C}$, $[\alpha]_D^{20} = +10.0^\circ$ ($c=0.6$, $d=2$, $\alpha = +0.12^\circ$, methanol). The obtained dextrorotatory acid (8.41 g, 0.03 mole), $[\alpha]_D^{20} = +10.0^\circ$, methanol) was mixed with 8.83 g (0.03 mole) cinchonidine and was dissolved in 200 ccm of 60 % acetone. The hot solution was filtered and allowed to stand at room temperature. After 24 h the first fraction of cinchonidine salt was filtered. Needles (9 g) m.p. $141-143^\circ\text{C}$

(decomp.), $[\alpha]_D^{20} = -51,7^\circ$ ($c=0,6$, $d=2$, $\alpha = -0,62^\circ$, methanol). After two crystallizations of the first fraction of the cinchonidine salt the product had physical properties which remained unchanged by further crystallization. Needles, m.p. 157-158°C (decomp.), $[\alpha]_D^{20} = -39,2^\circ$ ($c=0,6$, $d=2$, $\alpha = -0,47^\circ$, methanol), yield 3,5 g.

Analysis: For $C_{38}H_{42}N_2O_3$ (574,75) - Calcd: 4,9 % N; found: 5,0 % N

13. Dextrorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (13)

Cinchonidine salt 12 (3 g), (m.p. 157-158°C (decomp.), $[\alpha]_D^{20} = -39,2^\circ$, methanol) was converted into free acid according to ref [1]. The product (0,9 g) was crystallized from 75 % ethanol (10 ccm). Needles, m.p. 148-149°C, $[\alpha]_D^{20} = +49,2$ ($c=0,6$), $d=2$, $\alpha = +0,59^\circ$, methanol).

Analysis: For $C_{19}H_{20}O_2$ (280,35) - Calcd: 81,4 % C; 7,1 % H; found: 81,2 % C, 7,3 % H.

14. Amide of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (14)

Laevorotatory acid 11 (2,8 g) was converted into its amide as in section 5. The product (2,5 g) was crystallized from 90 % methanol (25 ccm). Needles, m.p. 122-123°C, $[\alpha]_D^{20} = -39,10$ ($c=0,6$, $d=2$, $\alpha = -0,47^\circ$, methanol), yield 0,4 g.

Analysis: For $C_{19}H_{21}NO$ (279,36) - Calcd: 5,0 % N; found: 5,2 % N.

15. Methylamide of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (15)

Laevorotatory acid 11 (2,8 g) was converted into its methylamide as in section 6. The crude product (2,2 g) was crystallized from 60 % ethanol (25 ccm). Plates, m.p. 142°C, $[\alpha]_D^{20} = -55,8^\circ$ ($c=0,6$, $d=2$, $\alpha = -0,67^\circ$, methanol), yield 1,5 g.

Analysis: For $C_{20}H_{23}NO$ (293,39) - Calcd: 4,8 % N; found: 4,9 % N.

16. Methylthioamide of laevorotatory 9-butyl-9-methylfluorene-2-carboxylic acid (16)

Methylamide 15 (2,25 g) (m.p. 142°C, $[\alpha]_D^{20} = -55,8^\circ$, methanol) was converted into methylthioamide as in section 7. The crude product (1,1 g) was crystallized from 90 % ethanol (15 ml). Pale yellow pla-

tes, m.p. 176°C $[\alpha]_{\text{D}}^{20} = -133.0^{\circ}$ ($c=0.5$, $d=2$, $\alpha = -1.33^{\circ}$, methanol),
yield 0.5 g.

Analysis: For $\text{C}_{20}\text{H}_{23}\text{NS}$ (309.46), Calcd: 4.5 % N, found: 4.5 % N.

UV/EtOH/ $\lambda_{\text{max}} = 200$ ($\epsilon = 19493.7$), 212 ($\epsilon = 23037.9$), 254 ($\epsilon = 5822.7$), 290 ($\epsilon = 19493.6$), 302 ($\epsilon = 18860.8$), 314 ($\epsilon = 21012.7$), 335 ($\epsilon = 8860.7$), 350 ($\epsilon = 3544.3$) nm.

17. *p*-Bromophenacyl ester of laevorotatory 9-butyl-9-methyl-
-fluorene-carboxylic acid (17)

Laevorotatory acid 11 (2.8 g) was converted into its *p*-bromo-
phenacyl ester analogously as in section 9. The crude product (2.5 g)
was crystallized from methanol (120 ml).

Needles, m.p. $96-97^{\circ}\text{C}$, $[\alpha]_{\text{D}}^{20} = -35.6^{\circ}$ ($c=0.8$, $d=2$, $\alpha = -0.57^{\circ}$,
2-butanone), yield 1.2 g.

Analysis: For $\text{C}_{27}\text{H}_{25}\text{BrO}_3$ (477.37) - Calcd: 67.9 % C, 5.3 % H;
found: 67.7 % C, 5.1 % H.

REFERENCES

1. Janczewski M., Matynia T., Roczniki Chem., 40, 2029 (1966), *ibid.* 45 2031 (1971).
2. Janczewski M., Matynia T., Ann. Univ. M. C. Skłodowska, Sec. AA, 28, 33 (1973).
3. Janczewski M., Pawłowska E., Roczniki Chem., 47, 665 (1973).
4. Janczewski M., Pawłowska E., Polish J. Chem., 54, 901 (1980).
5. Janczewski M., Pawłowska E., Ann. Univ. M. C. Skłodowska, Sec. AA, 34, 93 (1979).
6. Burakewich L., Djerassi C., J. Am. Chem. Soc., 87, 51 (1965).
7. Tschugaev L., Ber., 34, 360 (1898), *ibid.* 31, 1775 (1898).
8. Supniewski J., Preparatyka nieorganiczna, PWN, Warszawa, 480 (1958).
9. Murray J., Fritz H., pat. USA 3.192.277 (29.IV.1965); Chem. Abs., 63, 9894 (1965).

STRESZCZENIE

Opisano syntezę i podstawowe własności rac.kwasu 9-butylo-9-metylo-fluoreno-2-karboksylowego. Kwas racemiczny rozszczepiono w drodze krystalizacji frakcyjnej diastereomerycznych soli z optycznie czynnymi zasadami na enancjomery. Określono w rejonie $340 < \lambda < 600$ nm dyspersję rotacji optycznej lewoskrętnego enancjomeru, jego estrów i amidów. 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-butylo-9-metylo-fluoreno-2-karboksylowych z długościami fal optycznie czynnych pasm w nadfioletowej części widma.

РЕЗЮМЕ

Описали синтез и основные свойства рац. 9-бутил-9-метил-флюорендикарбоксылной кислоты. Рацемическую кислоту расщепляли путем фракционной кристаллизации диастереомерических солей с оптически деятельными щелочами на энантиомеры. Определили в пределах $340 < \lambda < 600$ nm дисперсию оптической ротации левовращающего энантиомера, его эфиров и амидов. На основе исследования спектров ORD и CD приписали отдельным антимерам относительные пространственные конфигурации. Установили двучленные уравнения, описывающие оптическую ротацию левовращающего энантиомера и его амида в нескольких растворителях в исследуемой области спектра. Показали совпадение численных величин дисперсионных постоянных, выступающих в двучленных уравнениях, определяющих оптическую ротацию энантиомерических 9-бутил-9-метил-флюорендикарбоксылных кислот с длинами волн оптически деятельных полос в ультрафиолетовой части спектра.