This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The synthesis and structure of 1,3,4-trisubstituted 2,5-dioxopyrrolidines and their behaviour in liquid crystalline systems

A. I. Galatina[a]; L. G. Derkach[a]; H. D. Kilimenchuk[a]; R. V. Kondratyeva[a]; N. S. Novikova[a]; Ju. K. Jarovoy[a]
[a] A. V. Bogatsky Physical-Chemical Institute of the National Academy of Sciences of Ukraine, 86 Lustdorfskaya doroga, 270080 Odessa, Ukraine,

Online publication date: 06 August 2010

To cite this Article Galatina, A. I. , Derkach, L. G. , Kilimenchuk, H. D. , Kondratyeva, R. V. , Novikova, N. S. and Jarovoy, Ju. K.(2000) 'The synthesis and structure of 1,3,4-trisubstituted 2,5-dioxopyrrolidines and their behaviour in liquid crystalline systems', Liquid Crystals, 27: 9, 1229 — 1233

To link to this Article: DOI: 10.1080/02678290050122088

URL: http://dx.doi.org/10.1080/02678290050122088

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 2000, VOL. 27, NO. 9, 1229–1233

The synthesis and structure of 1,3,4-trisubstituted 2,5-dioxopyrrolidines and their behaviour in liquid crystalline systems

A. I. GALATINA*, L. G. DERKACH, H. D. KILIMENCHUK,
R. V. KONDRATYEVA, N. S. NOVIKOVA and JU. K. JAROVOY

A. V. Bogatsky Physical-Chemical Institute of the National Academy of Sciences
of Ukraine, 86 Lustdorfskaya doroga, 270080 Odessa, Ukraine

(*Received 11 December 1998; in final form 14 March 2000; accepted 4 April 2000*)

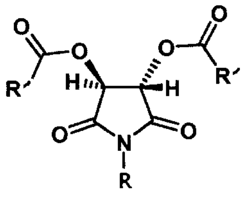
To find novel compounds for liquid crystalline mixtures with improved properties, a series of optically active 1,3,4-trisubstituted 2,5-dioxopyrrolidines has been prepared. Their structure was confirmed by IR spectroscopy. The twisting ability of the compounds prepared was studied.

1. Introduction

Many liquid crystal compounds are known which have six membered heterocyclic rings containing nitrogen: pyridines, pyrimidines, bipyridines, 1,2,4-triazines, etc. [1, 2]. With the purpose of obtaining novel effective materials, we have prepared compounds with the 2,5-dioxopyrrolidine ring in the structures of potentially mesogenic molecules. The series is obtained from (*R*,*R*)-(+)-tartaric acid and we have studied the changes in their mesogenic properties. The synthesis of these optically active cyclic 1,3,4-trisubstituted 2,5-dioxopyrrolidines extends the use of cyclic imides in the search for novel chiral dopants for liquid crystalline compositions for optoelectronic applications.

2. Synthesis of 1,3,4-trisubstituted 2,5-dioxopyrrolidines

The compounds (**13**–**21**) are of general formula



and were prepared by the reaction between the appropriate acid chlorides (**5**–**12**) and the *N*-substituted imides of (*R*,*R*)-(+)-tartaric acid (**1**–**4**) (see scheme 1).

The starting imides of (*R*,*R*)-(+)-tartaric acid were synthesized as a rule, by reactions based on the well known procedure of heating primary amines with (*R*,*R*)-(+)-tartaric acid [3]. This reaction required both high temperature and intensive stirring. The groups *R*′ were introduced through the acid chlorides *R*′COCl which were often derived from 4-substituted benzoic acids as their skeleton is mesogenic in nature [4].

The structures of all compounds prepared were carefully checked by elemental analysis, IR spectroscopy and NMR spectroscopy. For the *N*-substituted imides, two intense vibrational absorptions occur in the infrared region at 1780–1705 cm^{-1} corresponding to symmetric and antisymmetric carbonyl valence vibrations. Other characteristic frequencies of the imides prepared corresponded to data for analogous compounds described in [5]. The results were confirmed by the elemental analyses. These previously unreported esters (**13**–**21**) exhibited satisfactory elemental analyses and consistent spectral properties. In every instance intense vibrations were present in the IR region at 1735 cm^{-1} (carbonyl stretching) and at 1705 and 1606 cm^{-1} (phenyl ring vibration). The esters are colourless and their optical rotations were determined; the results are shown in the experimental section.

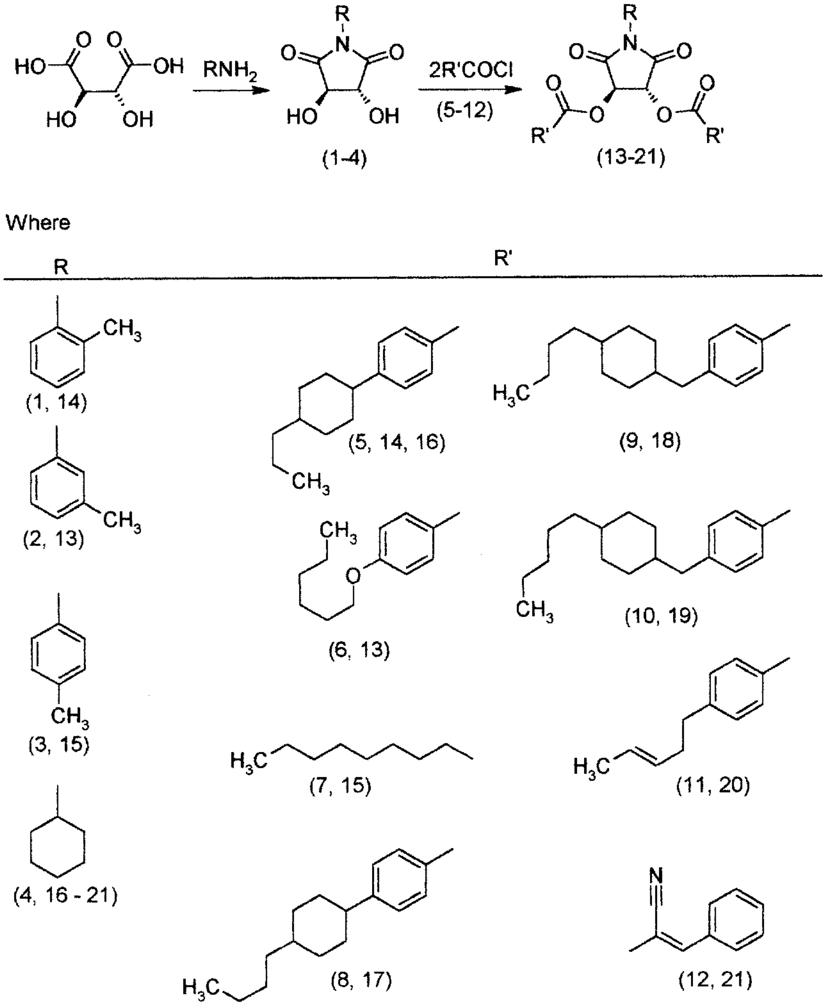
3. Behaviour of the 1,2,4-trisubstituted 2,5-dioxopyrrolidines in the liquid crystalline systems

Investigations of the 1,3,4-trisubstituted 2,5-dioxopyrrolidines mesogenic characteristics were carried out by polarizing microscopy. It was shown that the compounds prepared give no liquid crystal mesophases. However, they have a high optical activity and therefore an investigation of their ability to induce helical twisting in achiral liquid crystal compositions (twisting power) was undertaken. Two industrial compositions in which

---

*Author for correspondence; e-mail: physchem@paco.net

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
http://www.tandf.co.uk/journals



Scheme 1. Synthesis of the (*R*,*R*)-(+)-*N*-substituted-3,4-disubstituted-pyrrolidin-2,5-diones

the compounds investigated have a good solubility were used as achiral matrices. The first composition (matrix A) based on cyanobiphenyls has a very high polarity. The second matrix (matrix B) does not have a high polarity and is composed of phenylpyrimidines and has the transition temperatures shown below in scheme 2.

The twisting powers (β) of the dopants studied were measured in the nematic phase of matrix A at room temperature and in both the smectic C and nematic phases of matrix B at 40 and 60°C, respectively, which correspond to these phases. The results of the measurements are listed in the table and shown in figures 1 and 2.

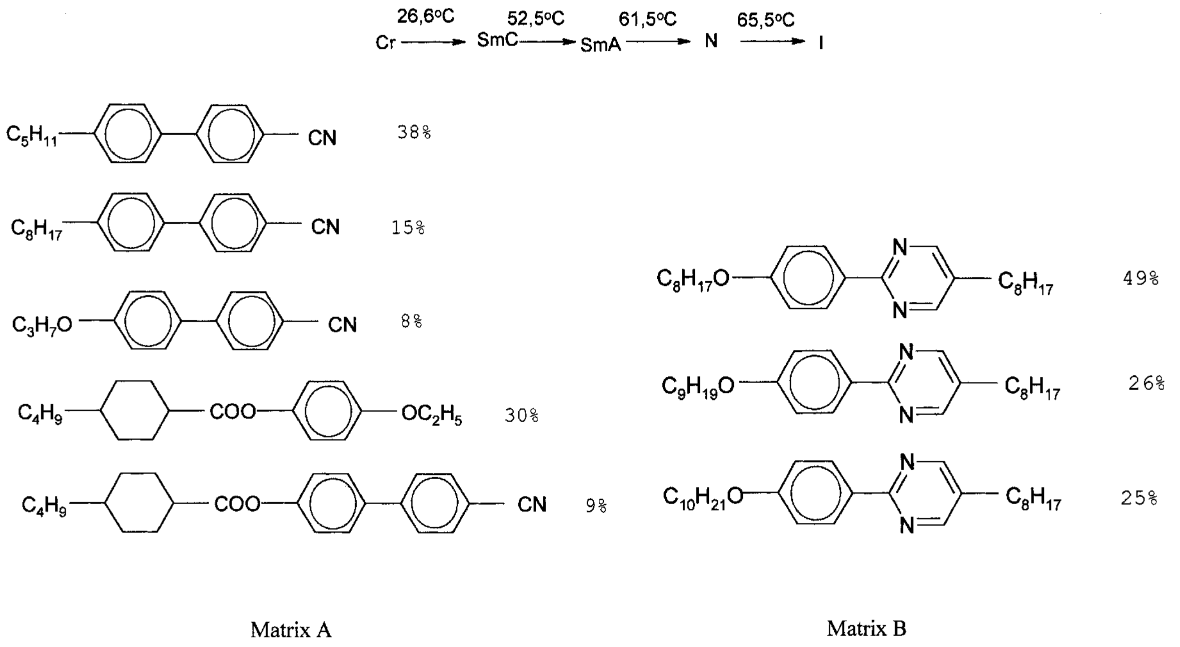
As can be seen from figures 1 and 2, the concentration dependences of the inverse helical pitch have a linear character for the range of concentrations of the chiral dopants investigated. The twisting power of all the dopants has an identical sign (the left helix is induced), but their values are different.

From the table and figures 1 and 2, the following points may be made.

(1) Compounds **16** and **17** which have the cyclohexyl group on the *N*-atom possess the highest values of the twisting power ($\beta_{17} = 0.237\ \mathrm{m\,km^{-1}/\%}$; $\beta_{16} = 0.220\ \mathrm{m\,km^{-1}/\%}$).

(2) The replacement of the cyclohexyl ring on the *N*-atom by the phenyl ring leads to considerable decrease of the twisting power (compounds **13**, **14** and **15**).

(3) A relatively small change of the actyl fragment, namely introduction of a $-CH_2-$ group between the cyclohexyl and phenyl rings, also decreases the β value ($\beta_{18} < \beta_{17}$). The twisting power values of the *N*-substituted 2,5-dioxopyrrolidines may now be compared to those of the well known commercial dopant 'Luch-15'—the (+)-2-methylheptyl ester of terphenyldicarboxylic acid (compound **22**) [7], dimethyl (2*R*,3*R*)-(+)-2,3-di-[4-(4-propylcyclohexyl)benzoyloxy]tartrate (compound **23**) and dimethyl (2*R*,3*R*)-(+)-2,3-di-(4-hexadecyloxybenzoyloxy)tartrate (compound **24**).



Scheme 2. Transition temperatures for matrix B and composition (wt %) of matrices A and B.

Table. Helical twisting power of some derivatives of (*R*,*R*)-(+)-tartaric acid in matrices A and B. N = nematic; SmC = smectic C.

Optically active dopant	Matrix	Mesophase	Twisting power β/ $\mathrm{m\,km^{-1}/\%}$
13	A	N	0.070
14	A	N	0.095
15	A	N	0.127
16	A	N	0.220
17	A	N	0.237
	B	N	0.167
	B	SmC	0.051
18	A	N	0.137
	B	N	0.125
	B	SmC	0.037
22	A	N	0.180
23	A	N	0.067
24	A	N	0.037
25	A	N	0.070
26	A	N	0.018

(4) As shown in the table and figure 1, the twisting powers of all the nitrogenous derivatives of tartaric acid are higher than the twisting power of the non-nitrogenous derivatives.

The β-values of derivatives of cholesterol namely cholesteryl perlargonate (**25**) and cholesteryl chloride (**26**) are also given in the table for comparison. As can be seen, the β-values of the derivatives of cholesterol are considerably lower than those of the compounds under study.

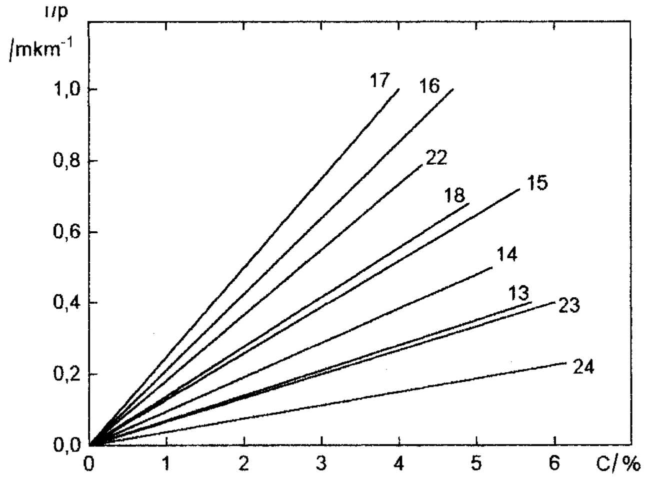


Figure 1. Dependence of the inverse helical pitch on the concentration of chiral dopant in matrix A. The line numbers correspond to compound numbers, whose composition is given in scheme 1 and § 3.

As also shown in figure 1, the concentration dependence of the *N*-containing derivatives of (*R*,*R*)-(+)-tartaric acid is generally higher than for the O-containing compounds just mentioned.

Special note should be taken of the results obtained using the smectic C phase of matrix B (figure 2). Besides the decrease of the β-value in comparison with the nematic phase by a factor of approximately three times more, entirely different threshold concentration values (C_0) arise for the same matrix depending on the molecular structure of the chiral dopant.

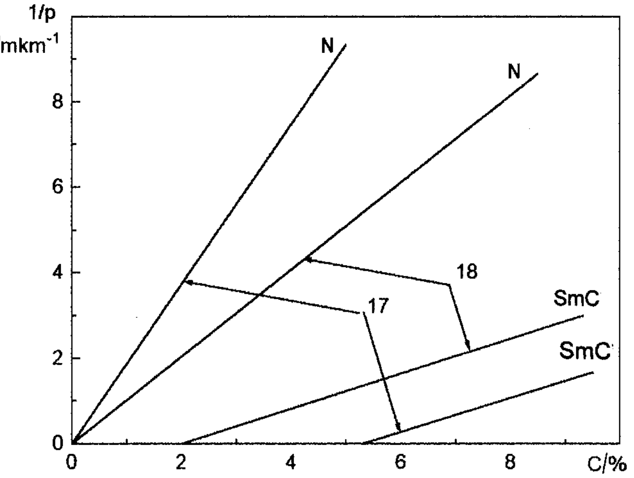


Figure 2. Dependence of the inverse helical pitch on the concentration of chiral dopant in the nematic and smectic phases of matrix B for the compounds **17** and **18**. (N = nematic phases, SmC = smectic phases).

For the compound **17** the threshold concentration is 5.5% and for compound **18** it is 2.5%. The threshold concentration values correlate with the degree of diminution of the twisting power values in the smectic phase as shown by the values of β_N and β_C in the table. The observed threshold character of formation of the helical structure in the smectic C phase, as well as the correlation between the threshold concentration and twisting power values in both phases, is in agreement with results of other work [8] and support the model of limited anisotropic chiral interactions in the smectic phase.

4. Experimental

4.1. *Analysis*

The compounds obtained were purified by column chromatography on neutral alumina or silica gel. Their purity was proved by thin layer chromatography.

Confirmation of the structures of the intermediates (imides of (*R*,*R*)-(+)-tartaric acid) was obtained by NMR spectroscopy (Bruker AM-250 MHz spectrometer) with tetramethylsilane as internal standard and by infrared spectroscopy (Specord-75 IR).

The specific rotations $[\alpha]_D^{20}$ were measured using a spectropolarimeter 'Polamat A' and 10 wt% solutions of the compounds in methanol, ethanol or chloroform.

The helical pitch measurements were made by the Cano method using a polarizing optical microscope 'Polam-P 320' and a cell with controlled heating.

4.2. *Synthesis of (3R,4R)-(+)-1-o-tolyl-3,4-dihydroxypyrrolidin-2,5-dione (1)*

To a rapidly stirred solution of (30.0 g, 0.2 mol) of (*R*,*R*)-(+)-tartaric acid in 10 ml of water (21.4 g, 0.2 mol) of *o*-toluidine was added dropwise at approximately 90°C. After the addition, the reaction mixture was heated for 5 h at 125–130°C. The resulting solid was crushed and crystallized from toluene. Purification by column chromatography on silica gel (eluent : hexane) afforded the desired (3*R*,4*R*)-(+)-1-*o*-tolyl-3,4-dihydroxypyrrolidin-2,5-dione (**1**), (63% yield), as a yellow crystalline solid, m.p. 189–190°C; $[\alpha]_D^{20} = +130$°C ($c = 10$ wt %, C_2H_5OH). Found, C 60.02, H 5.01, N 6.09; $C_{11}H_{11}NO_4$ requires C 59.73, H 4.98, N 6.33%. IR ν_{max}(KBr): 3200 (OH); 1775, 1710 (C=0 str.); 1260, 1010 (C–N) cm^{-1}. NMR: δ_H ($CDCl_3$): 2.27–2.38 (3H, s, CH_3), 4.58 (H, d, CH), 5.45 (H, d, OH), 7.1–7.5 (4H, m, C_6H_4) ppm.

4.3. *Synthesis of (3R,4R)-(+)-1-m-tolyl-3,4-dihydroxypyrrolidin-2,5-dione (2)*

(*R*,*R*)-(+)-Tartaric acid (30.0 g, 0.2 mol) was treated with *m*-toluidine (21.4 g, 0.2 mol) as described for the preparation of **1**—see § 4.2. Crystallization from ethanol–water (2 : 1) led to the desired product, (**2**) (47% yield), a yellow powder, m.p. 171°C; $[\alpha]_D^{20} = +180°$ ($c = 10$ wt %, C_2H_5OH). Found, C 59.92, H 5.03, N 6.12; $C_{11}H_{11}NO_4$ requires C 59.73, H 4.98, N 6.33%. IR: ν_{max}(KBr): 3550, 3400 (OH); 1775, 1705 (C=O); 1230, 1080 (C–N) cm^{-1}. NMR: δ_H ($CDCl_3$): 2.4 (3H, s, CH_3), 4.62 (H, d, CH), 6.4 (H, d, OH), 7.2–7.3 (4H, m, C_6H_4) ppm.

4.4. *Synthesis of (3R,4R)-(+)-1-p-tolyl-3,4-dihydroxypyrrolidin-2,5-dione (3)*

Compound (3) was prepared from (*R*,*R*)-(+)-tartaric acid (45.0 g, 0.3 mol) and *p*-toluidine (32.1 g, 0.3 mol) by the same procedure used for the preparation of compounds **1** and **2** in 82% yield, m.p. 269–272°C; $[\alpha]_D^{20} = +133°$ ($c = 10$ wt %, C_2H_5OH). Found, C 60.00, H 5.01, N 6.05; $C_{11}H_{11}NO_4$ requires C 59.73, H 4.98, N 6.33%. IR: ν_{max}(KBr): 3600, 1200 (OH); 1775, 1700 (C=O); 1200, 1050 (C–N) cm^{-1}. NMR: δ_H ($CDCl_3$): 2.38 (3H, s, CH_3), 4.55 (H, d, CH), 6.4 (H, d, OH), 7.4–7.33 (4H, dd, C_6H_{14}) ppm.

4.5. *Synthesis of (3R,4R)-(+)-1-cyclohexyl-3,4-dihydroxypyrrolidine-2,5-dione (4)*

The solid prepared from the reaction of (*R*,*R*)-(+)-tartaric acid and cyclohexylamine was crushed and purified twice by crystallization from ethanol/water (2 : 1). The desired imide (**4**) was obtained as a dark yellow crystalline solid in 38% yield, m.p. 183–184°C, $[\alpha]_D^{20} = +109.76°$ ($c = 10$ wt %, C_2H_5OH). Found, C 56.62, H 7.07, N 6.26; $C_{10}H_{15}NO_4$ requires C 56.34, H 7.04, N 6.57%. IR: ν_{max}(KBr): 3500 (OH), 1680 (C=O), 1240 (C–N) cm^{-1}.

4.6. *Synthesis of acid chlorides (**5–12**)*

The acid chlorides (**6**, **7**, **11**, **12**) were prepared by a well-known reaction [7] from the corresponding acid and an excess of thionyl chloride, isolating the products by removing the volatile excess of thionyl chloride. The residual acid chlorides were employed for the esterification reactions without additional purification. The acid chlorides **5**, **8**, **9**, **10** were prepared by the method of ref [4], by-passing the acid stage. Their analysis data are as follows:

*4-(4-Propylcyclohexyl)benzoyl chloride (**5**)*, 70% yield, m.p. 26°C. Found, C 72.00, H 7.58, Cl 14.00; $C_{16}H_{21}ClO$ requires C 72.57, H 7.89, Cl 13.70%.

*4-(4-Butylclohexyl)benzoyl chloride (**8**)*, 39% yield, b.p. 163°C/2 mm Hg. Found, C 73.31, H 8.31, Cl 12.89; $C_{17}H_{23}ClO$ requires C 73.25, H 8.26, Cl 12.75%.

*4-(Butylcyclohexylmethyl)benzoyl chloride (**9**)*, 60% yield, b.p. 158–160°C/2 mm Hg. Found, C 73.67, H 8.62, Cl 12.20; $C_{18}H_{25}ClO$ requires C 73.85, H 8.55, Cl 12.14%.

*4-(4-Pentylcyclohexylmethyl)benzoyl chloride (**10**)*, 42% yield, m.p. 30°C. Found, C 74.53, H 8.91, Cl 11.64; $C_{19}H_{27}ClO$ requires C 74.39, H 8.81, Cl 11.58%.

4.7. *Synthesis of (3R,4R)-(+)-1-substituted-3,4-disubstituted-pyrrolidin-2,5-diones (**13–21**)*

A solution of the acid chloride (**5**–**12**) (8.5 mmol) in 20 cm^3 dry diethyl ether was cooled to ~0°C. To this solution, with rapid stirring, a solution of the (3*R*,4*R*)-(+)-1-substituted-3,4-dihydroxypyrrolidin-3,5-dione (4.25 mmol) in dry pyridine (8.5 cm^3) was slowly added dropwise. The reaction mixture was then stirred at room temperature assessing the end of reaction by TLC (eluent: DMPA/chloroform, 3:1). The solvent was then removed under a slight vacuum and the residue taken up in ether. Following washes with water (three times), the ether layer was dried over $MgSO_4$ and the solvent evaporated. The residual product was crystallized from ethanol/water (3:1) and then from toluene. The resulting data are:

*(3R,4R)-(+)-1-m-tolyl-3,4-di-[4-hexyloxybenzoyloxy]-pyrrolidin-2,5-dione (**13**)*, 28% yield, as a white powder, m.p. 167–168°C, $[\alpha]_D^{20} = +66.5°$ (10 wt% in $CHCl_3$). Found, C 70.84, H 6.89, N 2.01; $C_{37}H_{43}NO_8$ requires C 70.59, H 6.84, N 2.22%. IR: (KBr): 1710, 1700, 1680, 1150 cm^{-1}.

*(3R,4R)-(+)-o-tolyl-3,4-di-[4-(4-propylcyclohexyl)-benzoyloxy]pyrrolidin-2,5-dione (**14**)*, (43% yield), as a white powder, m.p. 176°C, $[\alpha]_D^{20} = +65.3°$ (10 wt% in $CHCl_3$). Found, C 76.62, H 7.57, N 1.79; $C_{43}H_{51}NO_4$ requires C 76.21, H 7.53, N 2.06%. IR: ν_{max}(KBr) 1770, 1730, 1690 cm^{-1}.

*(3R,4R)-(+)-p-tolyl-3,4-dioctyloxypyrrolidin-2,5-dione (**15**)*, (41% yield), as a white powder, m.p. 45°C, $[\alpha]_D^{20} = +78.70°$ (10 wt% in methanol). Found, C 69.44, H 8.63, N 2.79; $C_{29}H_{43}NO_6$ requires C 69.46, H 8.58, N 2.79%. ν_{max}(KBr) 1765, 1730, 1700, 1160 cm^{-1}.

*(3R,4R)-(+)-1-cyclohexyl-3,4-di-[4-(4-propylcyclohexyl)benzoyloxy]pyrrolidine-2,5-dione (**16**)*, as a white powder, (57% yield), m.p. 220°C, $[\alpha]_D^{20} = +65.34°$ (10 wt% in $CHCl_3$). Found, C 75.80, H 82.26, N 1.81; $C_{42}H_{55}NO_6$ requires C 75.34, H 8.22, N 2.09%. ν_{max}(KBr) 1790, 1720, 1700, 1155 cm^{-1}.

*(3R,4R)-(+)-1-cyclohexyl-3,4-di-[4-(4-butylcyclohexyl)-benzoyloxy]pyrrolidine-2,5-dione (**17**)*, as a white powder, 41% yield, m.p. 161°C, $[\alpha]_D^{20} = +113.6°$ (10 wt% in $CHCl_3$). Found, C 76.15, H 8.51, N 1.69; $C_{44}H_{59}NO_6$ requires C 75.75, H 8.46, N 2.01%. ν_{max}(KBr) 1790, 1720, 1700, 1160 cm^{-1}.

*(3R,4R)-(+)-1-cyclohexyl-3,4-di-[4-(4-butylcyclohexylmethyl)benzoyloxy]pyrrolidine-2,5-dione (**18**)*, as a white powder, 51% yield, m.p. 138°C, $[\alpha]_D^{20} = +125.8°$ (10 wt% in $CHCl_3$). Found, C 76.49, H 8.74, N 1.61; $C_{46}H_{63}NO_6$ requires C 76.14; H 8.69, N 1.93%. ν_{max}(KBr) 1795, 1745, 1695, 1200 cm^{-1}.

*(3R,4R)-(+)-1-cyclohexyl-3,4-di-[4-(4-pentylcyclohexylmethyl)benzoyloxy]pyrrolidine-2,5-dione (**19**)*, as a white powder, 34% yield, m.p. 168°C, $[\alpha]_D^{20} = +78.25°$ (10 wt% in ethanol). Found, C 76.87, H 8.22, N 1.58; $C_{48}H_{67}NO_6$ requires C 76.49, H 8.90, N 1.86%. ν_{max}(KBr) 1785, 1710, 1690, 1200 cm^{-1}.

*(3R,4R)-(+)-1-cyclohexyl-3,4-di-[(4-pent-3-enyl)-benzoyloxy]pyrrolidine-2,5-dione (**20**)*, as a white powder, 44% yield, m.p. 40.8°C, $[\alpha]_D^{20} = +78°$ (10 wt% in $CHCl_3$). Found, C 73.62, H 7.04, N 2.23; $C_{34}H_{39}NO_6$ requires C 73.25, H 7.00, N 2.51%. ν_{max}(KBr) 1785, 1720, 1690, 1200 cm^{-1}.

*(3R,4R)-(+)-cyclohexyl-3,4-di-(3-phenyl-2-cyanoprop-2-enoyloxy)pyrrolidin-2,5-dione (**21**)*, as a white powder, 67% yield, m.p. 25.0°C, $[\alpha]_D^{20} = +88°$ (10 wt% in $CHCl_3$). Found, C 69.19, H 4.85, N 7.75; $C_{30}H_{25}N_3O_6$ requires C 68.85, H 4.78, N 8.03%.

References

[1] Grebonkin, M. F., and Ivashenko, I. V., 1989, *Dzidkokristallicheskiye Materiali, M* (Khimiya), pp. 26–28.

[2] Douce, L., and Liessel, R., 1995, *Liq. Cryst.*, **18,** 157.

[3] Sherowsky, G., and Schreiber, P., 1990, Pat. DE WP 3 822 121 A1.

[4] Demus, D., Frach, R., Deutscher, H.-I., and Zaschke, H., 1987, Pat. DDR WP 245 869.

[5] Ken, N., and Kodzi, H., 1990, Pat. Jap. 61-19633.

[6] Vladimirsky, I. V., Kondratyeva, R. V., Kramarenko, N. Z., and Schkabara, 1988, *Kristallographiya*, **33,** 701.

[7] Veigand-Hilgetag, 1968, *Metodi Experimenta v Organicheskoi Khimii*, p. 232.

[8] Wrobel, S., Hiller, S., and Haase, H., 1995, *Liq. Cryst.*, **18,** 21.