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Synthesis and Phase Behavior of Branched Esters Derived from Cyclohexylbenzoic Acid

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Abstract—A branched aldehyde on the basis of cyclohexylbenzoates and 3,5-dihydroxybenzoates was synthesized. For the characteristic of intermediates and the target substance TLC, elemental analysis, IR, NMR spectroscopy, and differential scanning calorimetry were used. It was found that at the increase in length and branching degree of aldehyde the final product acquires the tendency to transfer to the glassy state.

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Branched molecules are widely used in dendrimer chemistry [1, 2]. On their basis the macromolecules with the controlled structure and properties can be synthesized [3, 4] that permits to carry out microsegregation of final products with the formation of regular structures and giving the molecules spherical or the disk-like form [5, 6]. As a rule for this purpose the derivatives of gallic acid containing the long-chain aliphatic radicals ($C_{10}H_{21}$, $C_{12}H_{25}$, $C_{18}H_{37}$) are used. For the regular branching of the 1:3 type [7] the scheme of double increase in the dimensions of molecule is used taking 3,5-dihydroxybenzyl alcohol and its derivatives [8,9] as the branching center. Compounds of mixed nature containing cyclohexyl and aromatic fragment permit to give final products the new properties [10] which can not be acquired by the products constructed on the basis of classic approach using mono, di-, and trialkoxybenzoic acids. Due to that it presents interest to prepare aldehyde derived from cyclohexylbenzoic acid with the 1:2 branching on the basis of 3,5-dihydroxybenzoic acid. Such compounds, the derivatives of mono- and trialkoxybenzoates, are used for preparing of rare earth metal complexes with the luminescence and magnetic properties [11–13].

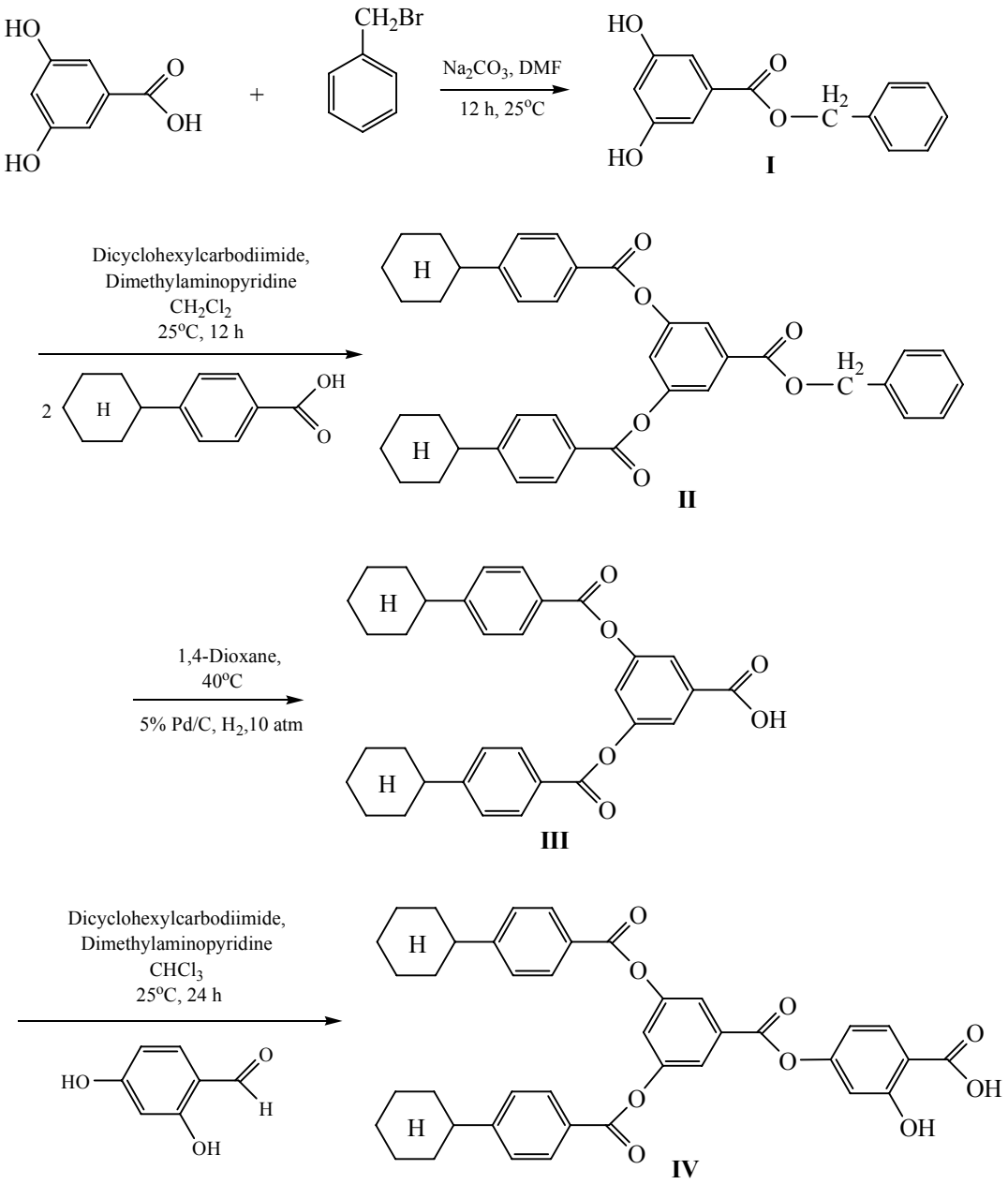
In the course of synthesis of 3,5-di(4-cyclohexylbenzoyl)oxybenzoyl-4-oxy-2-hydroxybenzaldehyde **IV** according to the scheme 1 the intermediates were prepared and studied.

For the subsequent branching of the target aldehyde 3,5-dihydroxybenzoic acid was chosen. The hydroxyl group location is sterically favorable for the further growth of molecules, and the carboxyl group can be easily exposed to chemical modifying. It permits to introduce benzyl fragment with the purpose of protecting the carboxyl group while preparing the branched molecule. Branching is achieved by formation of esterial groups. Protecting group is easily introduced in the molecule and easily removed from it without any alterations in the structure of the compound formed. Protected function is stable in presence of large number of reagents used for further transformations.

It was already mentioned previously that benzyl 3,5-dihydroxybenzoate can be used for the formation and removing protecting fragment in the course of synthesis of benzophenone fragments of medicinal remedies [14].

Benzyl 3,5-dihydroxybenzoate by itself can be the center of subsequent branching due to formation of esterial bonds between its hydroxyl groups and the carboxyl groups of any other reagents. It can be also the protecting block in the course of subsequent branching and chain elongation (Scheme 2).

Benzyl 3,5-dihydroxybenzoate **I** was prepared by us by means of alkylation of carboxyl group of 3,5-dihydroxybenzoic acid with benzyl bromide in dry



Scheme 1. Synthesis of 3,5-di[(4-cyclohexylbenzoyl)oxybenzoyl]-4-oxy-2-hydroxybenzaldehyde **IV.**

DMF. This compound was used further for the synthesis of branched benzyl 3,5-(cyclohexylbenzoyloxy)benzoate **II**. Removing of protecting group as toluene (debenzylation by hydrogenolysis) yielded free acid **III**. Esterification of the obtained 3,5-di(4-cyclohexylbenzoyl)oxybenzoic acid **III** with *p*-hydroxysalicylic aldehyde permitted to prepare the aldehyde **IV.**

Benzyl carboxylates are splitt with hydrogen on a palladium catalyst to form the corresponding carboxylic acids and toluene. Using of palladium catalyst for debenzylation in hydrogen medium gives good result, but this method is comparatively expensive and technologically complicated because it needs palladium salts, hydrogen of high purity, and the reactor with regulated pressure. That is why for removing the protective group we have tried to use the procedures reported by the workers [16–18]. Hence, for the case of 4-hydroxy-3-methoxyhydrocynnamic acid debenzylation accompanied by hydrogenation of the olefin double bond by treating with the HCl–

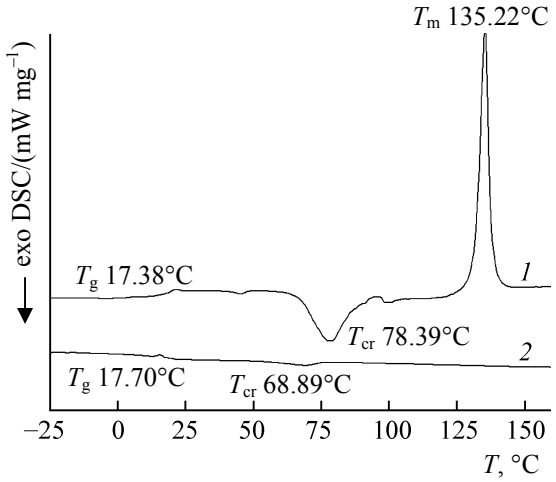
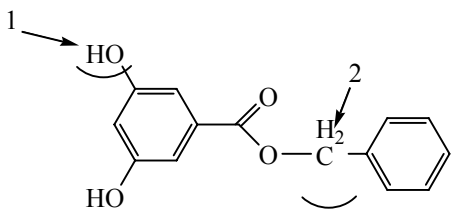


Fig. 1. Differential scanning calorimetry curves of benzyl 3,5-dihydroxybenzoate **I** in the cycles of heating and cooling. (*1*) Second heading and (*2*) first cooling.

CH_3COOH mixture was reported about [16]. In our case no reaction was observed even under the prolonged refluxing. Removing of benzyl group in a form of toluene by treating macrocycle esters with zinc powder and hydrochloric acid was described by the workers [17], but in the case of compound **II** this system occurred to be ineffective. Traditional hydrolysis of carboxylate by heating it in ethanolic KOH solution [18] was unsuccessful. Hence, using of Pd/H_2 system was the only suitable method for debenzylation of benzyl carboxylates in our case.

Phase behavior of compounds **I–IV** was studied by means of the differential scanning calorimetry. For the compound **I** (Fig. 1) its melting point was found to be 136.02°C. Note that while cooling the sample no crystallization was observed. Compound **I** remains in a glass-like state and demonstrates the melt–glass transfer unusual for the crystalline organic compounds (see the table). Such thermal behavior of compound can be explained by formation of stable intermolecular hydrogen bonds due to the interaction of the hydroxyl group protons of the 3,5-disubstituted aromatic ring. In the IR spectrum of this substance broad intense band in the range of the OH group vibrations is present. The



Scheme 2. Benzyl 3,5-dihydroxybenzoate **I**.

above-described proposal is confirmed also by the behavior of sample in the second heating. At the repeated heating from the glass-like state (T_g 17.38°C) the substance crystallizes at T_{cr} 78.39°C and melts subsequently at 135.22°C.

Compound **II** (Fig. 2) melts at 105.16°C with the subsequent vitrification at about 21.51°C on cooling. At the subsequent heating of the sample no glass-crystal transfer is observed. Phase behavior of the compound **III** is analogous to **II** with melting point 215.62°C and vitrification point ~65.51°C. Aldehyde **IV** is the hard white powder. Despite of that it demonstrates interesting phase behavior in the cycles of heating and cooling (Fig. 3).

In the first cycle of heating and cooling compound **IV** begins to crystallize at ~2.95°C with the subsequent malting at 64.91°C. Note that this compound does not remain in a melt, but transforms to the vitrified state at 168.34°C at the increase in temperature [19]. In the cycle of cooling the substance under study undergoes vitrification at 66.79°C giving the glass-glass transfer. In the second cycle of heating the aldehyde **IV** reveals only vitrification at 73.76°C. Such phase behavior can be explained probably by formation of intramolecular hydrogen bonds between the proton of hydroxyl group and the aldehyde group in the salicylic aldehyde fragment [20], and also by interaction of cyclohexane fragments.

EXPERIMENTAL

All the reagents and solvents were of "chemically pure" grade. They were used without the additional purification. IR spectra of compounds were recorded on a Bruker Vertex 80V device in the ranges 7500–370 cm^{-1} and 670–190 cm^{-1} in KBr and CsBr pellets. ^{1}H NMR (500.17 MHz) and ^{13}C NMR (125.78 MHz) spectra were taken on a Bruker Avance-500 spectrometer. Elemental analysis of crystalline substances was carried out on a FlashEA 1112 analyzer. Differential scanning calorimetry measurements were carried out on a NETZCH DSC 204 F1 device in the aluminum capsules. Mass of the batch ~10 mg, heating rate 10°C/min. Operations were performed under the nitrogen atmosphere. TLC was carried out on the PolyGRAM and Sil G/UV 254 plates, elution with chloroform. Chromatograms were developed by the UV irradiation at 254 nm.

Benzyl 3,4-dihydroxybenzoate (I). Freshly distilled benzyl bromide (25.33 ml) was mixed with

Temperatures of phase transfers according to the differential scanning calorimetry data

Comp. no.	Vitrification		Crystallizatio		Melting	
	T_g, °C	ΔC_{eq}, J g^{-1} K^{-1}	T_{cr}, °C	$-\Delta H_{cr}$, J g^{-1}	T_m, °C	ΔH_m, J g^{-1}
			Heating			
I	17.38	0.48	78.39	61.16	135.22	121.70
II	–	–	–	–	105.16	54.22
III	72.06	0.21	–	–	215.62	85.77
IV	158.34	0.17	–2.95	0.92	64.91	0.19
			Cooling			
I	17.70	0.41	68.89	5.71	–	–
II	21.51	0.23	–	–	–	–
III	65.51	0.23	–	–	–	–
IV	66.79	0.16	–	–	–	–

the solution of 3,5-dihydroxybenzoic acid (30 g) in dry DMF, and the batch of anhydrous Na_2CO_3 (20.64 g) was added to it. The mixture obtained was stirred for 12 h at room temperature under nitrogen. After that resulting brown solution was poured in 200 ml of distilled water and extracted with diethyl ether (5× 25 ml). Combined organic fractions were washed with water (3×25 ml), then with brine (20 ml), dried over the anhydrous Na_2SO_4 and concentrated in a vacuum. Solid residue was purified by crystallization from 1:6 dichloromethane-hexane mixture to give white crystals. Yield 42.49 g (89.3%), mp 135–136°C. IR spectrum, ν, cm^{-1}: 3387 s (OH group vibrations), 3028–3094 s (aromatic C–H), 2957 s (aliphatic CH_2), 1699 s (C=O), 1613 s (esterial –COO–), 1003 (flat deformational CH-vibrations of monosubstituted aromatic ring), 851 (1,3,5-substituted aromatic ring, non-planar deformational C–H vibrations). ^{1}H NMR spectrum [$(CD_3)_2CO$, TMS], δ, ppm: 5.33 s, (2H, CH_2), 6.61 s (1H, Ph–H), 7.06 s (2H, Ph–H), 7.41 m (5H, Ph–H), 8.94 s (2H, Ph–OH). ^{13}C NMR spectrum [$(CD_3)_2CO$, TMS], δ_C, ppm: 67.02 (–CH_2–), 108.78 (CH_{arom}, C^4,C^6), 128.87 (CH_{arom}, C^{12}), 129.23 (CH_{arom}, C^{11}, C^{13}, C^{19}, C^{14}), 132.90 (CH_{arom}, C^9, C^2), 137.27

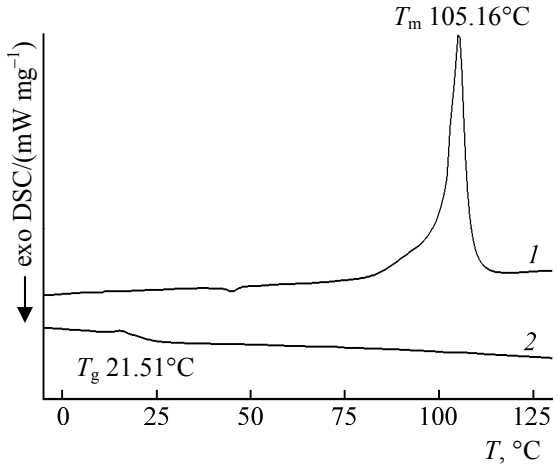


Fig. 2. Differential scanning calorimetry curves of benzyl 3,5-dicyclohexylbenzoyloxybenzoate in the cycles of heating and cooling. (*1*) First heading and (*2*) first cooling.

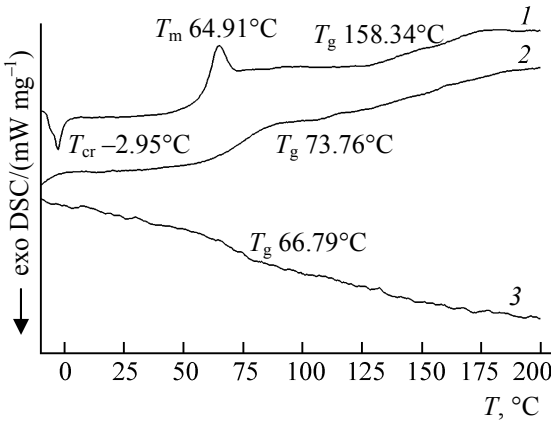


Fig. 3. Differential scanning calorimetry curves of the compound **IV** in the cycles of heating and cooling. (*1*) First heading, (*2*) second heating, and (*3*) first cooling.

(CH_{arom}, C^5), 159.56 (CH_{arom}, C^1, C^3), 166.76 (C=O). Calculated, %: C 68.85, H 4.95, O 26.20. $C_{14}H_{12}O_4$. Found, %: C 66.487, H 4.359, O 23.769.

Benzyl 3,5-di(4-cyclohexylbenzoyl)oxybenzoic acid (II). Batches of cyclohexylbenzoic acid (4 g), of compound **I** (2.39 g), and of dicyclohexylcarbodiimide (3.26 g) were dissolved in 100 ml of methylene chloride and stirred for 30 min. After that the catalytic amount of dimethylaminopyridine was added and the reaction mixture was stirred for 12 h. The urea formed was filtered off on a glass filter, and solvent was removed on a rotor evaporator. Dry yellow residue was chromatographed on silica gel, elution with chloroform. The target product is yellow oil crystallizing from 2:1 acetonitrile-chloroform mixture. Yield 3.73 g (30.88%), mp 105.16°C. IR spectrum, ν, cm^{-1}: 3096–3004 s (bond vibrations of the aromatic ring hydrogen atoms), 2924–2853 s (CH-aliphatic), 1742–1718 s (C=O vibrations), 1605 s (esterial –COO– vibrations), 1262–1218 s (asymmetric bond C–O–C vibrations), 1016–997 (–CH_2– vibrations of cyclohexane). ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.42 m (8H, $CH_2^{2,6}$-cyclohexyl), 1.88 m (8H, $CH_2^{3,5}$-cyclohexyl), 2.1 m (4H, CH_2^4-cyclohexyl), 5.36 s (2H, CH_2), 7.33 d (4H, $H^{2,5}$–Ph), 7.36 s (2H, $H^{4,4'}$–Ph), 7.38 m (2H, $H^{2,6}$-Ph), 7.42 d (2H, $H^{2,6}$-Ph), 7.83 m (2H, $H^{3,5}$-Ph), 8.09 d (4$H^{3,5}$–Ph). ^{13}C NMR spectrum ($CDCl_3$,TMS), δ_C, ppm: 25.95 ($CH_{2\text{-cyclohexyl}}$, C^{25}, C^{38}), 26.33 ($CH_{2\text{-cyclohexyl}}$ C^{26}, C^{24}, C^{39}, C^{37}), 33.97 ($CH_{2\text{-cyclohexyl}}$,C^{27}, C^{23}, C^{40}, C^{36}), 44.60 ($CH_{2\text{-cyclohexyl}}$, C^{22}, C^{35}), 67.20 (CH_2), 120.51 (CH_{arom} C^{12}), 120.75 (CH_{arom}, C^{14}, C^{10}, C^{21},C^{34}, C^{30}), 126.33(CH_{arom},C^{16}, C^{29}), 127.14 (CH_{arom}, C^{20}, C^{18}, C^{33},C^{31}), 128.31 (CH_{arom}, C^2, C^6), 128.57 (CH_{arom}, C^4), 130.32 (CH_{arom},C^3, C^5), 132.23 (CH_{arom},C^9), 151.23 (CH_{arom}, C^{13}, C^{11}) 154.55 (CH_{arom}, C^{19}, C^{32}), 164.52 (C=O, C^8, C^{15}, C^{28}). Calculated, %: C 77.90, H 6.54, O 15.57. $C_{40}H_{38}O_6$. Found, %: C 75.432, H 7.725, O 15.545.

3,5-Di(4-cyclohexylbenzoyloxy)benzoic acid (III). The calculated amount of catalyst, 5% Pd/C (0.36 g), was mixed with dioxane in a steel hydrogenation reactor and activated with hydrogen. After that a solution of 1 g of compound **II** in 100 ml of dioxane was added, and the reaction mixture was stirred at 40°C under hydrogen (10 ta) until the necessary amount of hydrogen, 16.2 mmol, was consumed. The reaction mixture was twice filtered through a glass filter, and solvent was removed on a rotor evaporator. The residue was crystallized from the 1:6 dioxane-hexane mixture. The solution was left on air until the formation of white crystals. Yield 0.7 g (70.1%), mp 216.26°C. IR spectrum, ν, cm^{-1}: 3461 w (OH bond vibrations), 3090 w (C–H aromatic bond vibrations), 2923–2650, 2599 s (CH_2 vibrations), 1742–1695 s (C=O vibrations), 1609 a (esterial –COO vibrations), 1256 s (asymmetric bond C–O–C vibrations), 1132 s (flat deformational C–H vibrations of the 1,4-disubstituted aromatic ring), 1057 s (flat deformational C–H vibrations of the 1,3,5-trisubstituted aromatic ring), 1016, 753–704 (m, cyclohexane –CH_2– vibrations). ^{1}H NMR spectrum ($CDCl_3$, TMS), δ, ppm: 1.22 d (2H, H-cyclohexyl), 1.38 m (8H, $CH_2^{2,6}$-cyclohexyl), 1.82 m (8H, $CH_2^{3,5}$-cyclohexyl), 2.54 m (4H, CH_2^4-cyclohexyl), 7.19 d (2H, Ph–$H^{2,6}$), 7.37 s (2H, Ph–H^4), 7.82 d (4H, Ph–$H^{3,5}$), 8.04 d (4H, Ph–$H^{2,6}$). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ_C, ppm: 25.85 ($CH_{2\text{-cyclohexyl}}$, C^{18}, C^{31}), 26.91 ($CH_{2\text{-cyclohexyl}}$, C^{19}, C^{17}, C^{32}, C^{30}), 34.29 ($CH_{2\text{-cyclohexyl}}$, C^{20}, C^{16}, C^{33}, C^{29}), 44.93 ($CH_{2\text{-cyclohexyl}}$, C^{15}, C^{28}), 121.06 (CH_{arom}, C^5), 121.57 (CH_{arom}, C^7, C^3, C^{14}, C^{10}, C^{27}, C^{23}), 126.37 (CH_{arom}, C^{13}, C^{11}, C^{26}, C^{24}), 127.26 (CH_{arom}, C^9, C^{22}), 130.54 (CH_{arom}, C^2), 151.46 (CH_{arom}, C^{12}, C^{25}), 154.75 (CH_{arom}, C^6, C^4), 164.56 (C=O, C^8, C^{21}), 169.90 (C=O C^1). Calculated, %: C 75.26, H 18.23, O 5.51. $C_{33}H_{34}O_8$. Found, %: C 75.512, H 6.907, O 18.26.

3,5-Di[(4-cyclohexylbenzoyloxy)benzoyl]-4-oxy-2-hydroxybenzaldehyde (IV). The batches of 4-hydroxysalicylic aldehyde, 0.47 g, of compound **III**, 1.8 g, and of dicyclohexylcarbodiimide, 1.92 g, were dissolved in 100 ml of chloroform during 30 min under stirring. After that the catalytic amount of dimethylaminopyridine was added, and the reaction mixture was stirred for 24 h. Precipitated urea was filtered off on a glass filter, solvent was removed on a rotor evaporator, and dry yellow residue was chromatographed on silica gel, elution with chloroform. The product, yellow oil, was crystallized from 10:1 acetonitrile–chloroform mixture. White powder, 0.96 g (43.37%) was obtained, mp 226°C. IR spectrum, ν, cm^{-1}: 3423 s (O–H bond vibrations), 2925 w (C–H bond vibrations of the aromatic rings), 2846, 2679-2534 w (CH_2-vibrations), 1729 s (Ar-COO vibrations), 1613 s (vibrations of the aromatic ring), 1388 s (vibrations of the aromatic aldehyde group), 1264 s (asymmetric bond C–O–C vibrations), 1131 s (flat deformational C–H vibrations of the 1,4-disubstituted aromatic ring), 1073 s (flat deformational C–H vibrations of the 1,3,5-trisubstituted aromatic ring), 998 w (CH_2 vibrations in cyclohexane). ^{1}H NMR spectrum, ($CDCl_3$, TMS), δ, ppm: 1.25 d (2H, H-

cyclohexyl), 1.42 m (8H, $CH_2^{2,6}$-cyclohexyl), 1.91 m (8H, $CH_2^{3,5}$-cyclohexyl), 2.60 m (4H, CH_2^4-cyclohexyl), 6.89 d (2H, Ph–$H^{2,6}$), 7.44 s (2H, Ph–H^4), 7.87 d (4H, Ph–$H^{3,5}$), 8.10 d (4H, Ph–$H^{2,6}$), 9.88 s (1H, CHO), 11.27 s (1H, Ph-OH). ^{13}C NMR spectrum ($CDCl_3$, TMS), δ_C, ppm: 25.85 ($CH_{2\text{-cyclohexyl}}$, C^{25}, C^{38}), 26.77 ($CH_{2\text{-cyclohexyl}}$, C^{26}, C^{24}, C^{39}, C^{37}), 34.23($CH_{2\text{-cyclohexyl}}$, C^{27}, C^{23}, C^{40}, C^{36}), 44.94 ($CH_{2\text{-cyclohexyl}}$, C^{22}, C^{31}), 120.98 (CH_{arom}, C^6, C^4), 121.20 (CH_{arom}, C^{12}), 126.35 (CH_{arom}, C^{13}, C^{11}), 127.00 (CH_{arom}, C^{21}, C^{17}, C^{34}, C^{30}), 127.21 (CH_{arom},C^{20}, C^{18}, C^{33}, C^{31}), 130.50 (CH_{arom}, C^9, C^{16}, C^{29}), 131.65 (CH_{arom}, C^7), 151.43 (CH_{arom}, C^{19}, C^{32}), 154.67 (CH_{arom}, C^5), 164.90 (C=O, C^{15}, C^{28}), 169.76 (C=O, C^8), 171.87 (CH_{arom}, C^{14}, C^{10}), 195.57 (CHO). Calculated, %: C 74.29; H 5.92, O 16.79. $C_{40}H_{38}O_8$. Found, %: C 75.03, H 7.16, O 18.9.

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REFERENCES

1. Balagurusami, V.S.K., Ungar, G., Percec, V., and Johansson, G., *J. Am. Chem. Soc*., 1997, vol. 119, p. 1539.
2. Lehmann, M., Schartel, B., Hennecke, M., and Meier, H., *Tetrahedron*, 1999, vol. 55, p. 13377.
3. Hawker, C.J. and Frechet, J.M.J., *J. Am. Chem. Soc*., 1990, vol. 112, p. 7638.
4. Freeman, A.W., Chrisstoffels, L.A.J., and Frechet, J.M.J., *J. Org. Chem*., 2000, vol. 65, p. 7612.
5. Lehmann, M., Gearba, R.L., Koch, M.H.J., and Ivanov, D.A., *Chem. Mater*., 2004, vol. 16, p. 374.
6. Cameron, J.H., Facher, A., Lattermann, G., and Diele, S., *Adv. Mater*., 1997, vol. 9, p. 398.
7. Tomalia, D.A., Naylor, A.M., and Goddard, III W.A., *Angew. Chem., Int. Ed. Engl*., 1990, vol. 29, p. 138.
8. Tully, D.C., Wilder, K., Frechet, J.M.J., Trimble, A.R., and Quate, C.F., *Adv. Mater*., 1999, vol. 11, no. 4, p. 314.
9. Saudan, C., Balzani, V., Gorka, M., Lee, S.-K., Maestri, M., Vicinelli, V., and Vugtle, F., *J. Am. Chem. Soc*., 2003, vol. 125, p. 4424.
10. Frolova, T.V., *Candidate Sci. (Chem.) Dissertation*, Ivanovo, 2005.
11. Galyametdinov, Yu., Athanassopoulou, M.A., Griesar, K., Kharitonova, O., Soto Bustamante, E.A., Tinchurina, L., Ovchinnikov, I., and Haase, W., *Chem. Mater*., 1996, vol. 8, p. 922.
12. Binnemans, K., Galyametdinov, Yu., Van Deun, R., Bruce, D.W., Collinson, S.R., Polishchuk, A.P., Bikchantaev, I., Haase, W., Prosvirin, A.V., Tinchurina, L., Litvinov, I., Gubaidullin, Aj., Rakhmatullin, Aj., Uytterhoefen, K., and Van Meerweit, L., *J. Am. Chem. Soc*., 2000, vol. 122, p 4335.
13. Barbera, J., Cavero, E., Lehmann, M., Serrano, J.-L., Sierra, T., and Vasquez, J.T., *J. Am. Chem. Soc*., 2003, vol. 125, p. 4527.
14. Denieul, M.P., Laursen, B., Hazell, R., and Skrydstrup, T., *J. Org. Chem*., 2000, vol. 65, p. 6052.
15. Shreenivasa Murthy, H.N. and Sadashina, B.K., *Liquid Crystals*, 2004, vol. 31, no. 10, p. 1347.
16. Titze, L. and Eicher, T., *Preparativnaya organicheskaya khimiya* (Preparative Organic Chemistry), Moscow: Mir, 1999.
17. McOmie, J.F.W., *Zashchitnye gruppy v organicheskoi khimii* (Protective Groups in Organic Chemistry), Moscow: Mir, 1976.
18. Weigand-Hilgetag, *Metody eksperimenta v organicheskoi khimii* (Experimental Methods in Organic Chemistry), Suvorov, N.N., Ed., Moscow: Khimiya, 1968.
19. Grazulevicius, J.V. and Strohriegl, P., *Handbook of Advanced Electronic and Photonic Materials and Devices*, Academic Press, 2000, vol. 10, p. 233.
20. Haddard, M.S., Lynch, M.W., Federer, W.D., and Heindrickson, D.N., *Inorg. Chem*., 1981, vol. 20, p. 123.