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Synthesis of New Mesogens of the 3-Arylisoxazolone and 3-Arylpyrazolone Series

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Abstract—Acylation of ethyl acetoacetate with mesogenic *para*-substituted benzoyl chlorides, followed by cleavage of ethyl aroylacetoacetates thus obtained under basic conditions, gave the corresponding ethyl 3-aryl-3-oxopropanoates which were brought into condensations with hydroxylamine and hydrazine to obtain mesogenic 3-arylisoxazolones and 3-arylpyrazolones, respectively.

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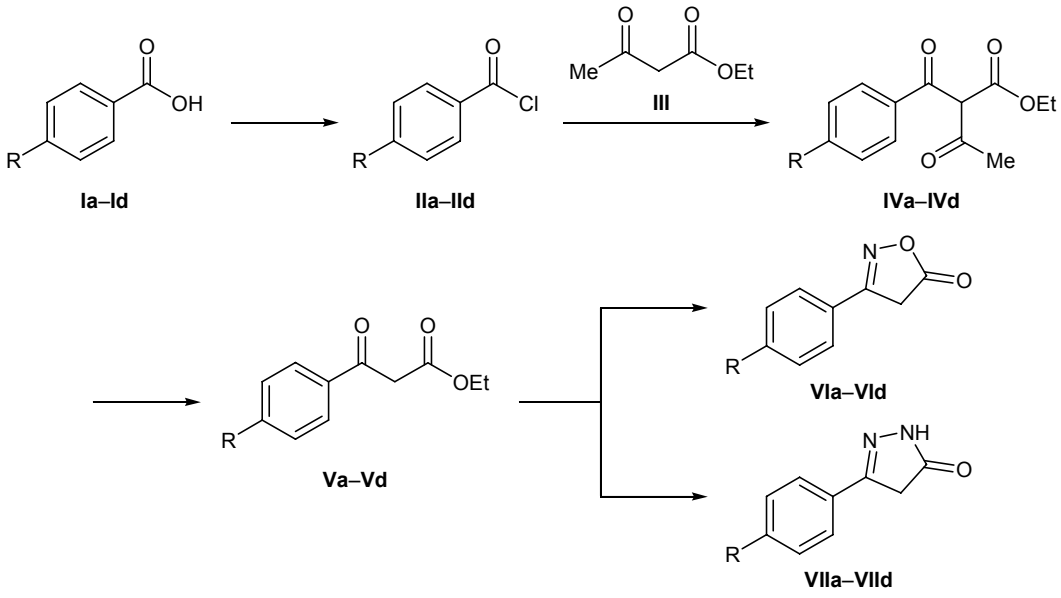
Liquid crystalline compounds possessing five-membered heterorings occupy a specific place among known classes of mesomorphic materials [1–7]. Such compounds can be used as components of smectic and nematic liquid crystalline systems characterized by good mesomorphic and electrooptical properties [1–7]. Liquid crystalline compounds containing various five-membered heterorings have been reported up to now [1–7]. In particular, we have synthesized a series of new mesogenic 4,5-dihydroisoxazole [7], isoxazole [8], and pyrazole derivatives [9]. Substituted isoxazol-5-ones and pyrazol-5-ones are structurally related to the above five-membered heterocyclic compounds.

Isoxazol-5-one and pyrazolo-5-one derivatives are well known as drugs, pesticides, materials for electronics, and analytical reagents [10–14]. Many substituted isoxazolones and pyrazolones were found to exhibit various kinds of biological activity [15, 16].

Scheme 1.



R = C_3H_7O (**a**), $C_7H_{15}O$ (**b**), $C_8H_{17}O$ (**c**), 4-$C_5H_{11}C_6H_4$ (**d**).

However, despite broad spectrum of practical applications of isoxazolones and pyrazolones, liquid crystalline compounds containing these five-membered heterocyclic fragments have not been reported so far. Taking the above stated into account, the goal of the present work was to synthesize mesogenic isoxazol-5-ones and pyrazol-5-ones and examine their mesomorphic properties. As first subjects for study we selected 3-arylisoxazolone and 3-arylpyrazolone derivatives.

The key intermediate products in the synthesis of isoxazolones and pyrazolones are substituted β-keto esters. The required ethyl 3-aryl-3-oxopropanoates **Va**–**Vd** were prepared by acylation of ethyl acetoacetate and subsequent cleavage according to Hunsdiecker [17] (Scheme 1). In the first step, 4-alkoxybenzoic acids **Ia**–**Ic** and 4′-pentylbiphenyl-4-carboxylic acid (**Id**) were converted into the corresponding benzoyl chlorides **IIa**–**IId** by treatment with thionyl chloride. Chlorides **IIa**–**IId** were used to acylate ethyl acetoacetate (**III**) in the presence of magnesium ethoxide. According to the TLC data, the reaction mixtures at that step contained β-oxo esters **Va**–**Vd** in addition to tricarbonyl compounds **IVa**–**IVd**. To avoid laborious separation of compounds **IV** and **V**, the product mixtures were subjected to cleavage under basic conditions without purification. This reaction was carried out using either aqueous ammonia in the presence of ammonium chloride or potassium hydroxide. The yields of target β-dicarbonyl compounds **V** attained 56% calculated on the initial benzoic acids.

The structure of β-keto esters **Va**–**Vd** was proved by their UV, IR, and ^{1}H NMR spectra. Compound **Vb** displayed in the UV spectrum an absorption maximum at λ 284 nm, which is typical of substituted benzene ring. The IR spectra of all compounds **Va**–**Vd** contained two strong carbonyl absorption bands (1634 and 1612 cm^{-1} for homologous compounds **Vb** and **Vc**). In the ^{1}H NMR spectra of **Va**–**Vd** we observed signals from protons in all structural fragments of their molecules (β-keto ester moiety, *para*-substituted benzene ring, and alkyl substituent). For instance, the ketone tautomer of **Va** showed in the ^{1}H NMR spectrum (CD_3OD) a multiplet signal at δ 3.31 ppm from the methylene protons in the 1,3-dicarbonyl fragment. In keeping with the ^{1}H NMR data, ester **Vb** in DMSO-d_6 exists exclusively in the enol form: the spectrum contained a singlet at δ 4.11 ppm due to the =CH proton in the enol fragment.

Mesogenic 3-arylisoxazol-5(4*H*)ones **VIa**–**VId** were synthesized in 90–95% yield by reaction of the corresponding β-keto esters **Va**–**Vd** with hydroxylamine hydrochloride in the presence of sodium acetate (Scheme 1). Their structure was confirmed by IR, UV, and NMR spectroscopy. In the UV spectrum of isoxazolone **VIb** we observed an absorption maximum at λ 280 nm. A small blue shift of the absorption maximum of compound **VIb** relative to that in the spectrum of β-keto ester **Vb** is likely to indicate that the corresponding electron transition occurs in the substituted benzene ring conjugated with the imino group. The IR spectra of isoxazolones **Va**–**Vd** contain strong absorption bands at 1819 and 1790 cm^{-1} due to stretching vibrations of the C=O and C=N bonds. In the ^{1}H NMR spectra of **VIa**–**VId**, methylene protons in the dihydroisoxazole ring resonated as a singlet at δ 3.90 ppm (2H), whereas no signals typical of ester ethoxy group (triplet and quartet) were present. These data confirmed the cyclization with formation of dihydroisoxazole ring and elimination of ethanol molecule.

The structure of isoxazolones **VIc** and **VId** was additionally confirmed by the ^{13}C NMR data. The ^{13}C NMR spectrum of **VIc** contained 15 signals, which is consistent with the formula $C_{17}H_{23}NO_3$ with account taken of magnetically equivalent carbon atoms in the benzene ring. The C=O and C=N signals appeared at δ_C 177.1 and 164.8 ppm, respectively, and the C^4 atom in the isoxazole ring resonated at δ_C 35.4 ppm.

Mesogenic 3-aryl-1*H*-pyrazol-5(4*H*)-ones **VIIa**–**VIId** were synthesized by reaction of β-keto esters **Va**–**Vd** with hydrazine hydrate, and their yields ranged from 66 to 95%. The structure of compounds **VIIa**–**VIId** unambiguously followed from their spectral data. The UV spectrum of **VIIb** contained an absorption maximum at λ 265 nm, whose position considerably differed from the position of the absorption maximum in the spectrum of initial β-keto ester **Vb**. All pyrazolones **VIIa**–**VIId** characteristically showed in the IR spectra broadened absorption bands in the regions 2000–2800 and 3300–3600 cm^{-1} due to stretching vibrations of the O–H and N–H groups involved in intermolecular hydrogen bonds. Stretching vibrations of the carbonyl group gave rise to a strong absorption band at 1619 cm^{-1}.

The ^{1}H NMR spectra of compounds **VIIa**–**VIId** were recorded from solutions in pyridine-d_5. Judging by the spectral data, pyrazolones **VIIa**–**VIId** in that solvent exist as 5-hydroxypyrazole or 2,5-dihydro-1*H*-pyrazol-5-one tautomers [10]. The spectra contained a one-proton signal at δ 6.33 ppm, which belongs to the vinylic 4-H proton; no signals assignable to meth-

ylene protons (C^4H_2) in the pyrazole ring and ethoxy group were present. The structure of compounds **VIIa**–**VIId** was also confirmed by their ^{13}C NMR spectra.

Study on mesomorphic properties of the obtained isoxazole and pyrazole derivatives showed that only compounds **VId** and **VIId** possessing a biphenyl fragment give rise to a mesophase. Isoxazolone **VId** was found to form monotropic nematic liquid crystalline phase with the following phase transition temperatures: heating: Cr→I (160°C); cooling: I→N (155°C)→Cr (147°C). Pyrazolone **VIId** produced smectic A phase in the temperature range from 270 to 292°C. Most probably, the lack of liquid crystalline properties of compounds **VIa**–**VIc** and **VIIa**–**VIIc** is related to small number of rings (2) in the rigid skeleton of their molecules.

EXPERIMENTAL

The melting points and phase transition temperatures were determined on a hot stage coupled with a polarizing microscope. Mesophases were identified by comparing the observed texture with reference samples given in [18]. The IR spectra (400–4000 cm^{-1}) were recorded in KBr (unless otherwise stated) on a Nicolet Nexus IR spectrometer with Fourier transform. The UV spectra were measured on a Specord M500 spectrophotometer. The NMR spectra were obtained on a Bruker Avance 500 instrument at 500.13 MHz for ^1H and 125.75 MHz for ^{13}C. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Kieselgel 60 F_{254} plates (Merck).

Ethyl 3-oxo-3-(4-propoxyphenyl)propionate (Va). A solution of magnesium ethoxide prepared from 4.35 g (181.2 mmol) of magnesium and 50 ml of anhydrous ethanol containing 5 ml of carbon tetrachloride was heated to the boiling point, and a solution of 22.9 ml (180.4 mmol) of ethyl acetoacetate in 40 ml of tetrahydrofuran was added dropwise under stirring. The mixture was cooled to 0°C, a solution of 4-propoxybenzoyl chloride [prepared from 32.46 g (180.3 mmol) of 4-propoxybenzoic acid and excess thionyl chloride] in 50 ml of tetrahydrofuran was added dropwise over a period of 30 min under stirring, and the mixture was stirred for 3 h on cooling with an ice bath and left overnight at room temperature. The mixture was then diluted in succession with 100 ml of water, 113 ml of dilute hydrochloric acid (10:1.3), and 100 ml of benzene. The aqueous phase was separated and extracted with benzene. The benzene extract was combined with the organic phase, washed with a saturated solution of sodium chloride, and evaporated under reduced pressure. The residue containing ethyl aroylacetoacetate **IVa** was dissolved in 50 ml of ethanol, a solution of 15.08 g (269.3 mmol) of potassium hydroxide was added, and the mixture was stirred for 24 h at room temperature, treated in succession with water and dilute hydrochloric acid (10:3), and extracted with benzene. The benzene extracts were washed with a saturated solution of sodium chloride and treated with neutral aluminum oxide over a period of 3 days. The sorbent was filtered off, the solvent was removed, and the residue was distilled under reduced pressure. A fraction of β-keto ester **Va** with bp 175–189°C (1 mm), 28.16 g, was additionally purified via conversion into the corresponding chelate with copper(II) acetate. Yield of **Va** 20.43 g (45%), n_D^{18} = 1.5330. IR spectrum, ν, cm^{-1} (film): 3077, 3045, 2970, 2939, 2879 (C–H); 1742, 1678 (C=O); 1601, 1574, 1511 (C=C_{arom}). ^1H NMR spectrum (CD_3OD), δ, ppm, ketone tautomer: 1.05 t (3H, CH_3, J = 7 Hz), 1.82 sext (2H, CH_2, J = 7 Hz), 4.02 t (2H, OCH_2, J = 7 Hz) {OC_3H_7}; 1.24 t (3H, CH_3, J = 7 Hz), 4.17 q (2H, OCH_2, J = 7 Hz) {OC_2H_5}; 3.31 m (2H, 2-H), 7.00 d (2H, H_{arom}, J = 9 Hz), 7.94 d (2H, H_{arom}, J = 9 Hz); enol tautomer: 1.30 t (3H, CH_3, J = 7 Hz), 3.98 t (2H, OCH_2, J = 7 Hz), 4.23 q (2H, OCH_2, J = 7 Hz), 6.95 d (2H, H_{arom}, J = 9 Hz), 7.75 d (2H, H_{arom}, J = 9 Hz).

Compounds **Vb**–**Vd** were synthesized in a similar way. In the synthesis of keto esters **Vc** and **Vd**, cleavage of ethyl aroylacetoacetates **IVc** and **VId** was performed using excess aqueous ammonia in the presence of ammonium chloride.

Ethyl 3-(4-heptyloxyphenyl)-3-oxopropionate (Vb). Yield 53%, mp 47–48°C (from propan-2-ol–petroleum ether). UV spectrum: λ_{max} 284 nm. IR spectrum, ν, cm^{-1}: 3048, 2956, 2940, 2866 (C–H); 1634, 1612 (C=O); 1573, 1516 (C=C_{arom}). ^1H NMR spectrum (DMSO-d_6), δ, ppm: enol tautomer (100%): 0.87 t (3H, CH_3, J = 7 Hz), 1.23–1.36 m (6H), 1.41 quint (2H, J = 7 Hz), 1.73 quint (2H, J = 7 Hz), 4.07 t (2H, OCH_2, J = 7 Hz) {OC_7H_{15}}; 1.18 t (3H, CH_3, J = 7 Hz), 4.11 q (2H, OCH_2, J = 7 Hz) {OC_2H_5}; 3.34 s (1H, OH, enol), 4.11 s (1H, 2-H), 7.05 d (2H, H_{arom}, J = 9 Hz), 7.92 d (2H, H_{arom}, J = 9 Hz).

Ethyl 3-(4-octyloxyphenyl)-3-oxopropionate (Vc). Yield 56%, mp 49–50°C (from propan-2-ol–petroleum ether). IR spectrum, ν, cm^{-1}: 3110, 3047, 2959, 2942, 2926, 2865, 2851 (C–H); 1634, 1612 (C=O); 1573, 1515 (C=C_{arom}). ^1H NMR spectrum

(CD_3OD), δ, ppm: ketone tautomer: 0.90 t (3H, CH_3, J = 7 Hz), 1.26–1.42 m (8H), 1.48 quint (2H, J = 7 Hz), 1.79 quint (2H, J = 7 Hz), 4.06 t (2H, OCH_2, J = 7 Hz) {OC_8H_{17}}; 1.24 t (3H, CH_3, J = 7 Hz), 4.17 q (2H, OCH_2, J = 7 Hz) {OC_2H_5}; 3.31 s (2H, 2-H), 6.99 d (2H, H_{arom}, J = 9 Hz), 7.94 d (2H, H_{arom}, J = 9 Hz); enol tautomer: 4.01 t (2H, OCH_2, J = 7 Hz), 4.23 q (2H, OCH_2, J = 7 Hz), 6.95 d (2H, H_{arom}, J = 9 Hz), 7.75 d (2H, H_{arom}, J = 9 Hz).

Ethyl 3-oxo-3-(4′-pentylbiphenyl-4-yl)propionate (Vd). Yield 22%, mp 105°C (from propan-2-ol–petroleum ether). UV spectrum: λ_{max} 309 nm. IR spectrum, ν, cm^{-1}: 3113, 2954, 2929, 2867, 2857 (C–H); 1645, 1615 (C=O); 1574, 1553, 1496 (C=C_{arom}). ^1H NMR spectrum (acetone-d_6), δ, ppm: ketone tautomer: 0.90 t (3H, CH_3, J = 7 Hz), 1.32–1.40 m (4H), 1.67 quint (2H, J = 7.5 Hz), 2.68 t (2H, $C_6H_4C\mathbf{H}_2$, J = 7.5 Hz) {C_5H_{11}}; 1.23 t (3H, CH_3, J = 7 Hz), 4.19 q (2H, OCH_2, J = 7 Hz) {OC_2H_5}; 4.14 s (2H, 2-H), 7.36 d (2H, H_{arom}, J = 9 Hz), 7.68 d (2H, H_{arom}, J = 9 Hz), 7.83 d (2H, H_{arom}, J = 9 Hz), 8.09 d (2H, H_{arom}, J = 9 Hz); enol tautomer: 4.28 q (2H, OCH_2, J = 7 Hz), 7.36 d (2H, H_{arom}, J = 9 Hz), 7.66 d (2H, H_{arom}, J = 9 Hz), 7.78 d (2H, H_{arom}, J = 9 Hz), 7.96 d (2H, H_{arom}, J = 9 Hz).

3-(4-Propoxyphenyl)isoxazol-5(4*H*)-one (VIa). A solution of 2.78 g (11.12 mmol) of keto ester **Va**, 0.85 g (12.2 mmol) of hydroxylamine hydrochloride, and 1.00 g (12.0 mmol) of sodium acetate in a mixture of 40 ml of ethanol and 10 ml of water was heated for 3 h under reflux with stirring. The mixture was then diluted with 50 ml of water, and the precipitate was filtered off and washed with aqueous ethanol (12 ml) and water (50 ml). Yield 1.94 g (92%), mp 118°C (from ethanol). UV spectrum, λ_{max}, nm: 266, 279. IR spectrum, ν, cm^{-1}: 3083 (C–H_{arom}); 2967, 2936, 2879 (C–H_{aliph}); 1818, 1790 (C=O, C=N); 1608, 1555, 1520 (C=C_{arom}); 1255, 1179 (C–O). ^1H NMR spectrum (CD_3CN), δ, ppm: 1.02 t (3H, CH_3, J = 7 Hz), 1.80 sext (2H, CH_2, J = 7 Hz), 3.90 s (2H, 4-H), 4.01 t (2H, OCH_2, J = 7 Hz), 7.01 d (2H, H_{arom}, J = 9 Hz), 7.64 d (2H, H_{arom}, J = 9 Hz).

Compounds **VIb**–**VId** were synthesized in a similar way.

3-(4-Heptyloxyphenyl)isoxazol-5(4*H*)-one (VIb). Yield 89%, mp 102°C (from propan-2-ol). UV spectrum: λ_{max} 280 nm. IR spectrum, ν, cm^{-1}: 3080 (C–H_{arom}); 2950, 2930, 2857 (C–H_{aliph}); 1819, 1790 (C=O, C=N); 1609, 1557, 1519 (C=C_{arom}); 1253, 1178 (C–O). ^1H NMR spectrum (CD_3CN), δ, ppm: 0.91 t (3H, CH_3, J = 7 Hz), 1.28–1.40 m (6H, CH_2), 1.45 quint (2H, CH_2, J = 7 Hz), 1.77 quint (2H, CH_2, J = 7 Hz), 3.90 s (2H, 4-H), 4.03 t (2H, OCH_2, J = 7 Hz), 7.01 d (2H, H_{arom}, J = 9 Hz), 7.64 d (2H, H_{arom}, J = 9 Hz).

3-(4-Octyloxyphenyl)isoxazol-5(4*H*)-one (VIc). Yield 96%, mp 108°C (from propan-2-ol). UV spectrum: λ_{max} 281 nm. IR spectrum, ν, cm^{-1}: 3079 (C–H_{arom}); 2923, 2854 (C–H_{aliph}); 1819, 1790 (C=O, C=N); 1609, 1592, 1558, 1519 (C=C_{arom}); 1252, 1177 (C–O). ^1H NMR spectrum (CD_3CN), δ, ppm: 0.89 t (3H, CH_3, J = 7 Hz), 1.24–1.40 m (8H, CH_2), 1.45 quint (2H, CH_2, J = 7 Hz), 1.76 quint (2H, CH_2, J = 7 Hz), 4.02 s (2H, 4-H), 4.03 t (2H, OCH_2, J = 7 Hz), 7.00 d (2H, H_{arom}, J = 9 Hz), 7.63 d (2H, H_{arom}, J = 9 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 14.43 (CH_3); 23.40, 26.69, 29.83, 30.02, 30.06, 32.61, 69.25 (CH_2); 35.40 (C^4); 116.01, 121.29, 129.42, 163.08 (C_{arom}); 164.82, 177.09 (C=N, C=O).

3-(4′-Pentylbiphenyl-4-yl)isoxazol-5(4*H*)-one (VId). Yield 90%. Phase transition temperatures: heating: Cr→I (160°C); cooling: I→N (155°C)→Cr (147°C). UV spectrum: λ_{max} 282 nm. IR spectrum, ν, cm^{-1}: 3085, 3049, 3024 (C–H_{arom}); 2954, 2920, 2855 (C–H_{aliph}); 1820, 1792 (C=O, C=N); 1607, 1588, 1502 (C=C_{arom}); 1176 (C–O). ^1H NMR spectrum (CD_3CN), δ, ppm: 0.90 t (3H, CH_3, J = 7 Hz), 1.29–1.40 m (4H, CH_2), 1.64 quint (2H, CH_2, J = 7.5 Hz), 2.66 t (2H, $C_6H_4C\mathbf{H}_2$, J = 7.5 Hz), 3.97 s (2H, 4-H), 7.32 d (2H, H_{arom}, J = 8 Hz), 7.61 d (2H, H_{arom}, J = 8 Hz), 7.78–7.80 m (4H, H_{arom}). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 14.39 (CH_3); 23.28, 31.98, 32.29, 36.10 (CH_2); 35.37 (C^4); 127.79, 127.95, 128.22, 128.33, 130.15, 137.86, 144.49, 145.17 (C_{arom}); 165.13, 176.93 (C=N, C=O).

3-(4-Propoxyphenyl)-1*H*-pyrazol-5(4*H*)-one (VIIa). β-Keto ester **Va**, 5.62 g (22.48 mmol), was dissolved in 40 ml of ethanol, 1.2 ml of hydrazine hydrate (containing 64% of hydrazine) was added, and the mixture was heated for 2 h 45 min under reflux. The mixture was cooled to room temperature and diluted with 40 ml of water, and the precipitate was filtered off and washed with 10 ml of aqueous ethanol (1:1) and 60 ml of water. Yield 4.29 g (88%), mp 229–230°C (from toluene–ethyl acetate). UV spectrum: λ_{max} 268 nm. IR spectrum, ν, cm^{-1}: 3500–2000 br (N–H); 3125 (C–H_{arom}); 2966, 2939, 2875 (C–H_{aliph}); 1619 (C=O); 1553, 1496 (C=C_{arom}); 1250, 1180 (C–O). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.83 t (3H, CH_3, J = 7 Hz), 1.59 sext (2H, CH_2, J = 7 Hz), 3.75 t (2H,

OCH_2, J = 7 Hz), 6.33 s (1H, 4-H), 7.00 d (2H, H_{arom}, J = 9 Hz), 7.88 d (2H, H_{arom}, J = 9 Hz). ^{13}C NMR spectrum (C_5D_5N), δ_C, ppm: 10.47 (CH_3); 22.68, 69.49 (CH_2); 87.07 (C^4); 115.17, 126.95 (C_{arom}); 159.26.

Compounds **VIIb**–**VIId** were synthesized in a similar way.

3-(4-Heptyloxyphenyl)-1*H*-pyrazol-5(4*H*)-one (VIIb). Yield 95%, mp 223°C (from propan-2-ol). UV spectrum: λ_{max} 265 nm. IR spectrum, ν, cm^{-1}: 2800–2000, 3600–3300 br (N–H); 3125 (C–H_{arom}); 2955, 2928, 2856 (C–H_{aliph}); 1619 (C=O); 1552, 1514, 1496 (C=C_{arom}); 1248, 1180 (C–O). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.76 t (3H, CH_3, J = 7 Hz), 1.06–1.19 m (6H, CH_2), 1.30 quint (2H, CH_2, J = 7 Hz), 1.63 quint (2H, CH_2, J = 7 Hz), 3.85 t (2H, OCH_2, J = 7 Hz), 6.34 s (1H, 4-H), 7.05 d (2H, H_{arom}, J = 9 Hz), 7.90 br.d (2H, H_{arom}, J = 9 Hz), 12.4–13.4 br.m (OH, NH). ^{13}C NMR spectrum (C_5D_5N), δ_C, ppm: 14.30 (CH_3); 22.90, 26.32, 29.33, 29.60, 32.03, 68.29 (CH_2); 87.27 (C^4); 115.40, 127.17 (C_{arom}); 159.52.

3-(4-Octyloxyphenyl)-1*H*-pyrazol-5(4*H*)-one (VIIc). Yield 85%, mp 208°C (from propan-2-ol). UV spectrum: λ_{max} 265 nm. IR spectrum, ν, cm^{-1}: 3600–3300, 2800–2000 br (N–H); 3123 (C–H_{arom}); 2924, 2855 (C–H_{aliph}); 1619 (C=O); 1553, 1496 (C=C_{arom}); 1248, 1181 (C–O). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.76 t (3H, CH_3, J = 7 Hz), 1.04–1.20 m (8H, CH_2), 1.30 quint (2H, CH_2, J = 7 Hz), 1.64 quint (2H, CH_2, J = 7 Hz), 3.85 t (2H, OCH_2, J = 7 Hz), 6.32 s (1H, 4-H), 7.04 d (2H, H_{arom}, J = 9 Hz), 7.88 d (2H, H_{arom}, J = 9 Hz). ^{13}C NMR spectrum (C_5D_5N), δ_C, ppm: 14.31 (CH_3); 22.93, 26.36, 29.52, 29.58, 29.63, 68.28 (CH_2); 87.28 (C^4); 115.38, 127.17 (C_{arom}); 159.53.

3-(4′-Pentylbiphenyl-4-yl)-1*H*-pyrazol-5(4*H*)-one (VIId). Yield 66%. Phase transition temperatures: Cr→SmA (270°C)→I (292°C). IR spectrum, ν, cm^{-1}: 3600–3250, 2800–2000 br (N–H); 3151, 3022 (C–H_{arom}); 2955, 2926, 2855 (C–H_{aliph}); 1616 (C=O); 1551, 1508 (C=C_{arom}). ^1H NMR spectrum (C_5D_5N), δ, ppm: 0.74 t (3H, CH_3, J = 7 Hz), 1.12–1.19 m (4H, CH_2), 1.49 quint (2H, CH_2, J = 7 Hz), 2.50 t (2H, $C_6H_4C\mathbf{H}_2$, J = 7 Hz), 6.43 s (1H, 4-H), 7.24 d (2H, H_{arom}, J = 8 Hz), 7.61 d (2H, H_{arom}, J = 8 Hz), 7.71 d (2H, H_{arom}, J = 8 Hz), 8.02 d (2H, H_{arom}, J = 8 Hz). ^{13}C NMR spectrum (C_5D_5N), δ_C, ppm: 14.23 (CH_3); 22.82, 31.47, 31.71, 35.73 (CH_2); 126.25, 127.19, 127.65, 129.50 (C_{arom}).

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