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Synthesis and Reactivity of Maleopimaric Acid *N*-Aryl(aralkyl)imidoamides

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Abstract—A method of synthesis of maleopimaric acid *N*-aryl(aralkyl)imidoamides by reaction of the corresponding aromatic amides of maleopimaric acid and amines in *p*-xylene at reflux was developed. Thermal stability of the synthesized compounds was evaluated by derivatography.

Keywords: rosin, aromatic amines, maleopimaric acid, amides, imidoamides

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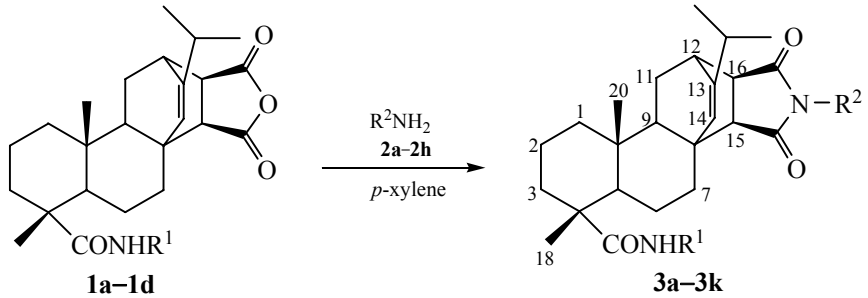
Among maleopimaric acid imidoamides aliphatic, cycloaliphatic and heterocyclic imidoamides some compounds exhibit hepatoprotective, immunomodulating and fungicidal activity [1–3]. Also aliphatic and aromatic polyimidoamides of maleopimaric acid of enhanced thermal stability [4–7] have known to be used as hydrophobic and anticorrosion coatings. However, data on aromatic imidoamides of maleopimaric acid are absent. As might be expected, the presence of *N*-aryl(aralkyl)amide and imide groups along with diterpenoid moiety in the molecule will improve the thermal stability of imidoamides in general providing a possibility to use such compounds in high temperature chemical processes, in particular, for modification of polymer and elastomer compositions. In addition, aromatic imidoamides as well as aliphatic and cycloaliphatic imidoamides may be of interest for the study of their biological activity.

The aim of this work was to develop a method of the synthesis of previously unknown *N*-aryl(aralkyl)-imidoamides of maleopimaric acid based on the reaction of aromatic amides of maleopimaric acid with amines. Aniline, *p*-toluidine, *p*-anisidine, *p*-fluoro-, *p*-chloro-, *p*-bromoaniline, benzylamine and 2-picolylamine were used as amines.

The reactions were performed by boiling a mixture of the corresponding amide **1** and amine **2** taken in a molar ratio of 1 : 3 in *p*-xylene for 40 h. Yield of the target imidoamides **3a**–**3k** reached 41–94% (Scheme 1).

Scheme 1.



1a–1d **3a–3k**

R^1 = C_6H_5 (**1a**), *p*-$CH_3C_6H_4$ (**1b**), *p*-BrC_6H_4 (**1c**), $CH_2C_6H_5$ (**1d**); R^1 = C_6H_5, R^2 = C_6H_5 (**2a**, **3a**), *p*-$CH_3C_6H_4$ (**2b**, **3b**), *p*-$MeOC_6H_4$ (**2c**, **3c**), *p*-FC_6H_4 (**2d**, **3d**), *p*-ClC_6H_4 (**2e**, **3e**), *p*-BrC_6H_4 (**2f**, **3f**), $CH_2C_6H_5$ (**2g**, **3g**), 2-picolyl (**2h**, **3h**); R^1 = *p*-$CH_3C_6H_4$, R^2 = *p*-$CH_3C_6H_4$ (**2i**, **3i**); R^1 = *p*-BrC_6H_4, R^2 = *p*-BrC_6H_4 (**2j**, **3j**); R^1 = $CH_2C_6H_5$, R^2 = $CH_2C_6H_5$ (**2k**, **3k**).

Carrying out the reaction at a lower temperature (reflux in toluene) and using 20–100% excess of amine led to a considerable decrease in the yield of the reaction products. Thus, reaction of maleopimaric acid anilide **1a** with aniline **2a** (molar ratio of 1 : 1.2, boiling in toluene for 40 h) produced imidoamide **3a** in 20% yield, whereas the use of *p*-xylene under similar conditions provided 31% yield of compound **3a**. Use of double excess of aniline relative to the amide **1a** (*p*-xylene, reflux, 40 h) made it possible to increase the yield of imidoamide **3a** up to 50%, and only using a threefold excess of aniline imidoamide **3a** was obtained in a yield of 70%. This dependence of the yield of target imidoamides **3a**–**3k** on the amount of aromatic amines **2a–2h** was apparently due to growing reaction rate owing to higher concentration of amine in the reaction mixture and the increased polarity of the system in general [8].

The obtained imidoamides **3a**–**3k** were colorless crystalline substances soluble in dimethyl formamide, dimethyl sulfoxide, and poorly soluble in methanol, diethyl ether, and hydrocarbons. Their structure was confirmed by elemental analysis, IR, NMR, and mass spectra. According to ^{1}H NMRdata the purity of the compounds obtained was 99±1%.

The IR spectra of compounds **3a**–**3k** contained characteristic absorption bands of amide group at 1680±10 (amide I) and 1595±5 cm^{-1} (amide II) and no absorption bands of anhydride C=O group (1780, 1840 cm^{-1}). In addition, there was an absorption due to stretching vibrations of C=O bond in the ranges of 1774±6 and 1704±7 cm^{-1}, characteristic of the imide ring of maleopimaric acid [9, 10]. The ^{1}H NMR spectra of aromatic imidoamides **3a**–**3k** contained the signals of amide fragment of maleopimaric acid [11, 12], as well as the signals of the protons of aryl substituents of the imide group. In the ^{13}C NMR spectra of compounds **3a**–**3l** the number of signals corresponded to the number of carbon atoms in aromatic imidoamides of maleopimaric acid. The mass spectra contained molecular ion peak $[M + 1]^+$.

Derivatography method [13] was used to estimate the thermal stability of compounds **3a**, **3d–3g**, **3j**, and **3k**. Imidoamides **3a**, **3d**, **3e**, **3g** were thermally stable and started to decompose with a significant rate in the temperature range of 325–335°C, which is by 30–40°C higher than the decomposition temperature of the starting anilide of maleopimaric acid **1a** and by 40–50°C higher than the decomposition temperature of maleopimaric acid (285°C). *N*-(*p*-Bromophenyl)imide of maleopimaric acid anilide **3e** has a lower thermal stability (310°C), and replacing maleopimaric acid anilide **1a** by *p*-bromophenylamide **1c** in imidoamide **3k** resulted in a significant decrease in its thermal stability (decomp. at 250°C). Thermal stability of **3k** was comparable to that of imidoamides **3a**, **3d**, **3e**, and **3g** (decomp. at 325°C).

EXPERIMENTAL

IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer from KBr pellets. ^{1}H NMR and ^{13}C spectra were registered on an AVANCE 500 spectrometer (500 and 125 MHz, respectively) for solutions in $CDCl_3$ (**3a**–**3i**, **3k**) and DMSO-d_6 (**3j**). Chemical shifts were determined relative to residual solvent signals. Mass spectra were obtained on an Accela mass spectrometer with LCQ Fleet detector in chemical ionization mode (APCI) with positive ion detection. Elemental analysis was performed on a VARIO Micro Cube CHNS analyzer. Thermal stability of synthesized aromatic imidoamides was studied on a NETZSCH STA 449 F1 derivatograph in an argon atmosphere with a linear temperature rise at a rate of 5 deg min^{-1}.

The starting maleopimaric acid anilide **1a** was obtained as described in [14]; *p*-methylphenylamide **1b**, and benzylamide **1c** and maleopimaric acid *p*-bromoanilide were prepared by the procedure reported in [11].

Aromatic imidoamides of maleopimaric acid (3a–3k). A mixture of 1 g (2.1 mmol) of maleopimaric acid anilide **1a**, 6.3 mmol of an appropriate amine **2a**–**2h**, and 5 mL of *p*-xylene was refluxed with a Dean–Stark trap for 40 h and then left standing for 48 h at room temperature. The resulting precipitate was filtered off, washed with *p*-xylene (3 × 1 mL) and air-dried. In the case of compound **3g** to the reaction mixture was added 15 mL of toluene, the mixture was washed with 10% HCl solution (2 × 10 mL), water (3 × 10 mL), dried with Na_2SO_4, and evaporated. In the case of imidoamide **3h** to the reaction mixture was added 25 mL of toluene, the mixture was washed with water (5 × 30 mL), dried with Na_2SO_4, and evaporated; the residue was evacuated at 125°C and 2 mmHg for 1 h.

Maleopimaric acid imidoamides **3i**–**3k** were prepared similarly from 1.8–2.0 mmol of amides **1b**–**1d** and 5.4–6.0 mmol of amine **2b**, **2f**, **2g**. Compounds

3i and **3k** were isolated from the reaction mixture similarly to the procedure of the synthesis of imidoamides **3a**–**3f**, imidoamide **3k,** by the procedure for isolation of compound **3g**.

***N*-Phenylimide of maleopimaric acid anilide (3a).** Yield 0.81 g (70.0%), mp 248–250°C. IR spectrum, ν, cm^{-1}: 2960, 1780, 1711 [(C=O)N], 1692 [(C=O)N], 1600, 1527 (C=C_{Ar}), 1311 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 1.01 d [3H, $(C\underline{H}_3)_2CH$, *J* = 6.0 Hz], 1.03 d [3H, $(C\underline{H}_3)_2CH$, *J* = 6.0 Hz], 1.06 m (1H, $C^{18}H_3$), 1.60 m (1H, $C^{18}H_3$), 1.32 s (1H, $C^{18}H_3$), 1.42–1.62 m (8H), 1.76 m (2H), 1.90 m (2H), 2.29 sextet [1H, $(CH_3)_2C\underline{H}$, *J* = 6.0 Hz), 2.60 m (2H, C^7H_{eq}, $C^{15}H$), 2.98 d.d (1H, $C^{16}H$, *J* = 8.0, 3.0 Hz), 3.18 br.s (1H, $C^{12}H$), 5.53 s (1H, $C^{14}H$), 7.13 m (3H, H_{Ar}), 7.34 m (3H, H_{Ar}), 7.42 m (2H, H_{Ar}), 7.49 s (1H, NH), 7.54 d (2H, H_{Ar}, *J* = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.79, 17.08, 17.17, 20.10, 20.82, 21.37, 27.59, 32.79, 35.25, 36.13, 36.98, 37.86, 40.98, 45.01, 47.59, 49.93, 52.38, 54.06, 120.19, 124.36, 124.52, 126.42, 128.39, 128.95, 129.02, 131.93, 137.80, 147.26, 176.28, 176.75, 177.60. Mass spectrum, *m*/*z*: 551 $[M + 1]^+$. Found, %: C 78.07; H 7.80; N 5.30. $C_{36}H_{42}N_2O_3$. Calculated, %: C 78.37; H 7.86; N 5.08.

***N*-(*p*-Methylphenyl)imide of maleopimaric acid anilide (3b).** Yield 1.02 g (85.9%), mp 297–298°C. IR spectrum, ν, cm^{-1}: 2953, 1769, 1702 [(C=O)N], 1674 [(C=O)N], 1598, 1516 (C=C_{Ar}), 1310 (C−N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 1.00 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.04 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.06 m (1H), 1.30 m (1H), 1.32 s (3H, $C^{18}H_3$), 1.40–1.62 m (8H), 1.73–1.81 m (2H), 1.89–2.00 m (2H), 2.29 sextet [1H, $(CH_3)_2C\underline{H}$, *J* = 7.0 Hz], 2.35 s (3H, $C\underline{H}_3C_6H_4$), 2.58 m (2H, C^7H_{eq}, $C^{15}H$), 2.97 d.d (1H, $C^{16}H$, *J* = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 5.52 s (1H, $C^{14}H$), 6.98 d (2H, H_{Ar}, *J* = 8.0 Hz), 7.13 m (1H, H_{Ar}), 7.21 d (2H, H_{Ar}, *J* = 8.0 Hz), 7.34 m (2H, H_{Ar}), 7.47 s (1H, NH), 7.54 d (2H, H_{Ar}, *J* = 8.0 Hz). Mass spectrum, *m*/*z*: 565 $[M + 1]^+$. Found, %: C 78.75; H 8.05; N 4.79. $C_{37}H_{44}N_2O_3$. Calculated, %: C 78.69; H 7.85; N 4.96.

***N*-(*p*-Methoxyphenyl)imide of maleopimaric acid anilide (3c).** Yield 1.03 g (83.7%), mp 291–292°C. IR spectrum, ν, cm^{-1}: 2953, 1767, 1701 [(C=O)N], 1674 [(C=O)N], 1597, 1513 (C=C_{Ar}), 1308 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 1.00 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.04 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.06 m (1H), 1.31 m (1H), 1.33 s (3H, $C^{18}H_3$), 1.37–1.62 m (8H), 1.77 m (2H), 1.88–2.00 m (2H), 2.29 sextet [1H, $(CH_3)_2C\underline{H}$, *J* = 7.0 Hz], 2.58 m (2H, C^7H_{eq}, $C^{15}H$), 2.96 d.d (1H, $C^{16}H$, *J* = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 3.80 s (3H, CH_3O), 5.52 s (1H, $C^{14}H$), 6.92 d (2H, H_{Ar}, *J* = 9.0 Hz), 7.02 d (2H, H_{Ar}, *J* = 9.0 Hz), 7.13 m (1H, H_{Ar}), 7.35 m (2H, H_{Ar}), 7.47 s (1H, NH), 7.54 d (2H, H_{Ar}, *J* = 9.0 Hz). Mass spectrum, *m*/*z*: 581 $[M + 1]^+$. Found, %: C 76.36; H 7.71; N 4.61. $C_{37}H_{44}N_2O_4$. Calculated, %: C 76.52; H 7.64; N 4.82.

***N*-(*p*-Fluorophenyl)imide of maleopimaric acid anilide (3d).** Yield 0.75 g (62.9%), mp 264–266°C. IR spectrum, ν, cm^{-1}: 2956, 1771, 1705 [(C=O)N], 1672 [(C=O)N], 1597, 1510 (C=C_{Ar}), 1309 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 0.99 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.02 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.06 m (1H), 1.31 m (1H), 1.33 s (3H, $C^{18}H_3$), 1.37–1.65 m (8H), 1.73–1.82 m (2H), 1.92–2.00 m (2H), 2.28 sextet [1H, $(CH_3)_2C\underline{H}$, *J* = 7.0 Hz], 2.57 m (1H, C^7H_{eq}), 2.60 d (1H, $C^{15}H$, *J* = 8.0 Hz), 2.97 d.d (1H, $C^{16}H$, *J* = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 5.52 s (1H, $C^{14}H$), 7.11 m (5H, H_{Ar}), 7.35 m (2H, H_{Ar}), 7.48 s (1H, NH), 7.54 d (2H, H_{Ar}, *J* = 8.0 Hz). Mass spectrum, *m*/*z*: 569 $[M + 1]^+$. Found, %: C 76.04; H 7.29; N 4.95. $C_{36}H_{41}FN_2O_3$. Calculated, %: C 76.03; H 7.27; N 4.93.

***N*-(*p*-Chlorophenyl)imide of maleopimaric acid anilide (3e).** Yield 0.50 g (40.7%), mp 272–274°C. IR spectrum, ν, cm^{-1}: 2955, 1770, 1704 [(C=O)N], 1673 [(C=O)N], 1597, 1524 (C=C_{Ar}), 1309 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 0.99 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.03 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.05 m (1H), 1.31 m (1H), 1.33 s (3H, $C^{18}H_3$), 1.39–1.70 m (8H), 1.70–1.81 m (2H), 1.90–1.99 m (2H), 2.70 sextet [1H, $(CH_3)_2C\underline{H}$, *J* = 7.0 Hz], 2.56 m (1H, C^7H_{eq}), 2.60 d (1H, $C^{15}H$, *J* = 8.0 Hz), 2.98 d.d (1H, $C^{16}H$, *J* = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 5.52 s (1H, $C^{14}H$), 7.01–7.14 m (3H, H_{Ar}), 7.33–7.39 m (4H, H_{Ar}), 7.48 s (1H, NH), 7.54 d (2H, H_{Ar}, *J* = 8.0 Hz). Mass spectrum, *m*/*z*: 585 $[M + 1]^+$. Found, %: C 73.29; H 7.20; N 5.01. $C_{36}H_{41}ClN_2O_3$. Calculated, %: C 73.89; H 7.06; N 4.79.

***N*-(*p*-Bromophenyl)imide of maleopimaric acid anilide (3f).** Yield 0.89 g (67.1%), mp 273–274°C. IR spectrum, ν, cm^{-1}: 2955, 1771, 1705 [(C=O)N], 1672 [(C=O)N], 1597, 1524 (C=C_{Ar}), 1309 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.68 s (3H, $C^{20}H_3$), 0.98 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.01 d [3H, $(C\underline{H}_3)_2CH$, *J* = 7.0 Hz], 1.05 m (1H), 1.31 m (1H), 1.33 s (3H, $C^{18}H_3$), 1.38–1.65 m (8H), 1.73–1.81 m (2H), 1.88–2.00 m

(2H), 2.70 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz], 2.56 m (1H, C^7H_{eq}), 2.60 d (1H, $C^{15}H$, J = 8.0 Hz), 2.98 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 5.52 s (1H, $C^{14}H$), 7.03 d (2H, H_{Ar}, J = 9.0 Hz), 7.13 m (1H, H_{Ar}), 7.35 m (2H, H_{Ar}), 7.47 s (1H, NH), 7.53 d (4H, H_{Ar}, J = 8.0 Hz). Mass spectrum, m/z: 630 $[M + 1]^+$. Found, %: C 68.64; H 6.84; N 5.06. $C_{36}H_{41}BrN_2O_3$. Calculated, %: C 68.67; H 6.56; N 4.45.

***N*-Benzylimide of maleopimaric acid anilide (3g).** Yield 1.00 g (84.2%), mp 189–190°C. IR spectrum, ν, cm^{-1}: 2928, 1768, 1696 [(C=O)N], 1674 [(C=O)N], 1597, 1523 (C=C_{Ar}), 1310 (C–N). ^1H NMR spectrum, δ, ppm: 0.62 s (3H, $C^{20}H_3$), 0.66 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.86 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 1.02 m (1H), 1.23 m (1H), 1.31 s (3H, $C^{18}H_3$), 1.36–1.60 m (6H), 1.62–1.78 m (4H), 1.84–1.96 m (2H), 2.02 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz], 2.44 d (1H, $C^{15}H$, J = 8.0 Hz), 2.53 m (1H, C^7H_{eq}), 2.80 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 3.05 br.s (1H, $C^{12}H$), 4.47 m (2H, $C\underline{H}_2C_6H_5$), 5.30 s (1H, $C^{14}H$), 7.13 m (1H, H_{Ar}), 7.22–7.30 m (5H, H_{Ar}), 7.35 m (2H, H_{Ar}), 7.45 s (1H, NH), 7.53 d (2H, H_{Ar}, J = 8.0 Hz). Mass spectrum, m/z: 565 $[M + 1]^+$. Found, %: C 78.72; H 8.14; N 4.64. $C_{37}H_{44}N_2O_3$. Calculated, %: C 78.69; H 7.85; N 4.96.

***N*-(2-Picolyl)imide of maleopimaric acid anilide (3h).** Yield 1.12 g (94.2%), mp 128–129°C. IR spectrum, ν, cm^{-1}: 2954, 1771, 1700 [(C=O)N], 1674 [(C=O)N], 1595, 1523 (C=C_{Ar}), 1310 (C–N). ^1H NMR spectrum, δ, ppm: 0.45 s (3H, $C^{20}H_3$), 0.65 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.73 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.84 m (1H), 1.08 m (1H), 1.12 s (3H, $C^{18}H_3$), 1.16–1.43 m (8H), 1.46–1.62 m (2H), 1.66–1.80 m (2H), 1.96 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz), 2.35 m (2H, $C^{15}H$, C^7H_{eq}), 2.70 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 2.91 br.s (1H, $C^{12}H$), 4.47 m (2H, $C\underline{H}_2C_5H_4N$), 5.23 s (1H, $C^{14}H$), 6.86–6.95 m (3H, H_{Ar}), 7.08–7.19 m (2H, H_{Ar}), 7.32–7.44 m (4H, H_{Ar}), 8.32 s (1H, NH). Mass spectrum, m/z: 566 $[M + 1]^+$. Found, %: C 75.71; H 7.46; N 5.91. $C_{36}H_{43}N_3O_3$. Calculated, %: C 76.43; H 7.66; N 7.43.

***N*-(4-Methylphenyl)imide of maleopimaric acid 4-methylphenylamide (3i).** Yield 0.98 g (82.9%), mp 271–272°C. IR spectrum, ν, cm^{-1}: 2955, 1770, 1703 [(C=O)N], 1670 [(C=O)N], 1595, 1517 (C=C_{Ar}), 1311 (C–N). ^1H NMR spectrum, δ, ppm: 0.67 s (3H, $C^{20}H_3$), 1.00 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 1.03 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 1.05 m (1H), 1.29 m (1H), 1.31 s (3H, $C^{18}H_3$), 1.36–1.60 m (7H), 1.86–1.98 m (3H), 1.86–1.98 m (2H), 2.29 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz], 2.33 s (3H, $C\underline{H}_3C_6H_4$), 2.35 s (3H, $C\underline{H}_3C_6H_4$), 2.58 m (2H, $C^{15}H$, C^7H_{eq}), 2.96 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 3.17 br.s (1H, $C^{12}H$), 5.52 s (1H, $C^{14}H$), 6.99 d (2H, H_{Ar}, J = 8.0 Hz), 7.14 d (2H, H_{Ar}, J = 8.0 Hz), 7.21 d (2H, H_{Ar}, J = 8.0 Hz), 7.41 d (2H, H_{Ar}, J = 8.0 Hz), 7.43 s (1H, NH). Mass spectrum, m/z: 579 $[M + 1]^+$. Found, %: C 77.82; H 8.00; N 4.57. $C_{38}H_{46}N_2O_3$. Calculated, %: C 78.86; H 8.01; N 4.84.

***N*-(4-Bromophenyl)imide of maleopimaric acid 4-bromophenylamide (3j).** Yield 0.98 g (76.7%), mp 243–245°C. IR spectrum, ν, cm^{-1}: 2957, 1773, 1705 [(C=O)N], 1673 [(C=O)N], 1589, 1514 (C=C_{Ar}), 1327 (C–N). ^1H NMR spectrum, δ, ppm: 0.60 s (3H, $C^{20}H_3$), 0.91 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.92 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 1.03 m (1H), 1.17 m (3H, $C^{18}H_3$), 1.20 m (2H), 1.36–1.60 m (8H), 1.72–1.86 m (3H), 2.16 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz], 2.38 m (1H, C^7H_{eq}), 2.66 d (1H, $C^{15}H$, J = 8.0 Hz), 2.97 br.s (1H, $C^{12}H$), 3.06 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 5.51 s (1H, $C^{14}H$), 7.01 d (2H, H_{Ar}, J = 9.0 Hz), 7.47 d (2H, H_{Ar}, J = 9.0 Hz), 7.62 d (2H, H_{Ar}, J = 9.0 Hz), 7.66 d (2H, H_{Ar}, J = 9.0 Hz), 9.30 s (1H, NH). Mass spectrum, m/z: 709 $[M + 1]^+$. Found, %: C 61.05; H 6.24; N 3.79. $C_{36}H_{40}Br_2N_2O_3$. Calculated, %: C 61.03; H 5.69; N 3.95.

***N*-Benzylimide of maleopimaric acid benzylamide (3k).** Yield 1.08 g (91.4%), mp 91–93°C. IR spectrum, ν, cm^{-1}: 2925, 1768, 1696 [(C=O)N], 1639 [(C=O)N], 1519 (C=C_{Ar}), 1314 (C–N). ^1H NMR spectrum, δ, ppm: 0.39 s (3H, $C^{20}H_3$), 0.46 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.65 d [3H, $(C\underline{H}_3)_2CH$, J = 7.0 Hz], 0.80 m (1H), 0.97 s (3H, $C^{18}H_3$), 1.03 m (1H), 1.11 m (1H), 1.15–1.36 m (7H), 1.44–1.58 m (2H), 1.61 m (1H), 1.69 m (1H), 1.82 sextet [1H, $(CH_3)_2C\underline{H}$, J = 7.0 Hz], 2.23 d (1H, $C^{15}H$, J = 8.0 Hz), 2.34 m (1H, C^7H_{eq}), 2.59 d.d (1H, $C^{16}H$, J = 8.0, 3.0 Hz), 2.84 br.s (1H, $C^{12}H$), 4.30 m (4H, $C\underline{H}_2C_6H_5$), 5.10 s (1H, $C^{14}H$), 7.04–7.19 m (11H, H_{Ar}, NH). Mass spectrum, m/z: 579 $[M + 1]^+$. Found, %: C 78.42; H 8.02; N 4.28. $C_{38}H_{46}N_2O_3$. Calculated, %: C 78.86; H 8.01; N 4.84.

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