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Efficient Synthesis of Maleopimaric Acid *N*-Arylimides

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Abstract—An efficient approach toward synthesis of maleopimaric acid *N*-arylimides starting from rosin maleic anhydride adduct without isolation of maleopimaric acid has been elaborated. Terpenoid diimide diacids and their esters have been synthesized based on the obtained *N*-arylimides. Thermal stability of the products has been estimated by derivatography.

Keywords: rosin, aromatic amine, maleopimaric acid, imide, ester

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One of the promising applications of renewable wood-chemical raw materials is synthesis of certain valuable chemicals. The best accessible individual terpenoid compound isolated from adduct of rosin (product of pine turpentine treatment) with maleic anhydride is maleopimaric acid **I**, a convenient synthon for preparation of compounds possessing a wide range of useful properties and application. Aliphatic amides, imides, and amide-imides have been the described among nitrogen-containing derivatives of maleopimaric acid [1–4]; the compounds have shown a set of valuable properties such as hepatoprotective [2], nematicidal [3], fungicidal, and bactericidal [4] activities. Only a few representatives of acid **I** aromatic imides have been known; for example, 4-aminophenyl imide [5] converted into thermally stable poly(amido)imides [6], *N*-(2-methyl-α-naphthyl)imide displaying antineoplastic activity [7], and 4-carboxyphenyl imide prepared from levopimaric acid and *p*-carboxyphenylmaleic acid imide [8]. At the same time, aromatic imides as well as aliphatic imides may possess diverse biological activity. Since maleopimaric acid is an accessible chiral acid, it may be used for separation of optical isomers of amines [9] provided that the labile anhydride group is converted into the fragment inert towards amines. Maleopimaric acid *N*-arylimides serve as suitable substrates.

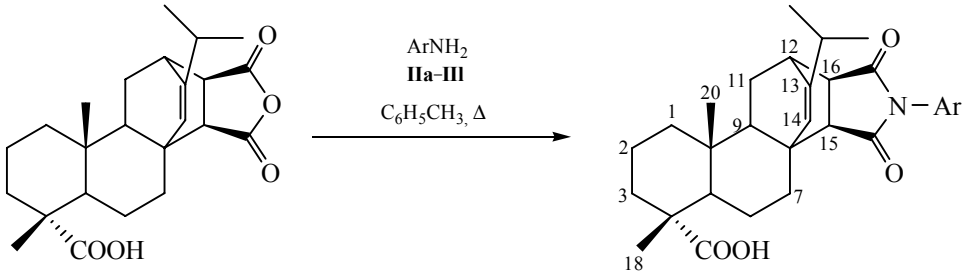
Maleopimaric acid 4-phenyl-(4-methyl-, 4-hydroxy-, 4-bromo-, 4-amino-, 3-amino-, and 3-carboxyphenyl)imides have been prepared earlier [10] via refluxing of a mixture of individual acid **I** with the corresponding amine (taken in 10 mol % excess or in equimolar amount) in toluene or pyridine. Reaction of 3- and 4-aminophenylimides with substituted benzaldehydes of vanillin series afforded biologically active azomethines [11, 12].

This work aimed to elaborate an efficient method of synthesis of maleopimaric acid *N*-arylimides **IIIa–IIIl** from accessible adduct of rosin with maleic anhydride and aromatic amines **IIa–IIl** without isolation of individual acid **I** (refluxing in toluene during 40 h). The rosin–maleic anhydride adduct with content of maleopimaric acid **I** of about 57% was prepared via treatment of rosin with maleic anhydride [13, 14].

Under the elaborated conditions, maleopimaric acid **I** as a component of the adduct reacted with aromatic amines **IIa–IIl** via the anhydride group to form exclusively *N*-arylimides **IIIa–IIIl** as insoluble precipitates that could be easily separated off the unreacted tar acids, well soluble in toluene. Such preparation of *N*-arylimides avoided the stage of maleopimaric acid isolation, allowing to significantly reduce the process duration and amount of the consumed organic solvents; the target imides could be isolated in 51–71% (with respect to rosin–maleic anhydride adduct) or 60–99% (with respect to maleopimaric acid contained in the rosin–maleic anhydride adduct) yield (Scheme 1).

The synthesized imides were colorless (**IIIa–IIIc**, **IIIf–IIIk**) or slightly colored (**IIId**, **IIIe**, **IIIl**) solids

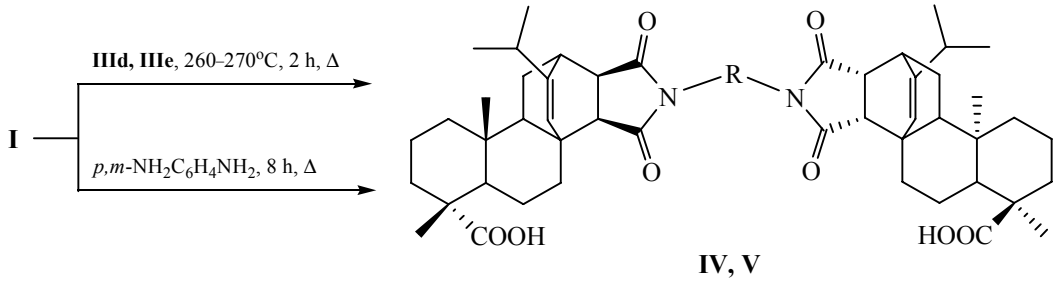
Scheme 1.



I **IIIa–IIIl**

Ar = C_6H_5 (**a**), *p*-$C_6H_4CH_3$ (**b**), *o*-$C_6H_4CH_3$ (**c**), *p*-$C_6H_4NH_2$ (**d**), *m*-$C_6H_4NH_2$ (**e**), *p*-C_6H_4OH (**f**), *p*-$C_6H_4OCH_3$ (**g**), *p*-C_6H_4F (**h**), *p*-C_6H_4Cl (**i**), *m*-C_6H_4Cl (**j**), *p*-C_6H_4Br (**k**), *p*-C_6H_4I (**l**).

Scheme 2.



IV, V

R = 1,4-C_6H_4 (**IV**), 1,3-C_6H_4 (**V**).

practically insoluble in majority of organic solvents (benzene, toluene, THF, diethyl ether, acetone, and DMF) and partially (up to 2–5%) soluble in DMSO; solubility of *p*-iodophenylimide **IIIl** in DMSO was of 25%.

Structures of imides **IIIa–IIIl** were confirmed by elemental analysis, IR and ^{1}H NMR spectroscopy, and mass spectrometry data. According to ^{1}H NMR spectroscopy, purity of the prepared compounds was of 98±1%.

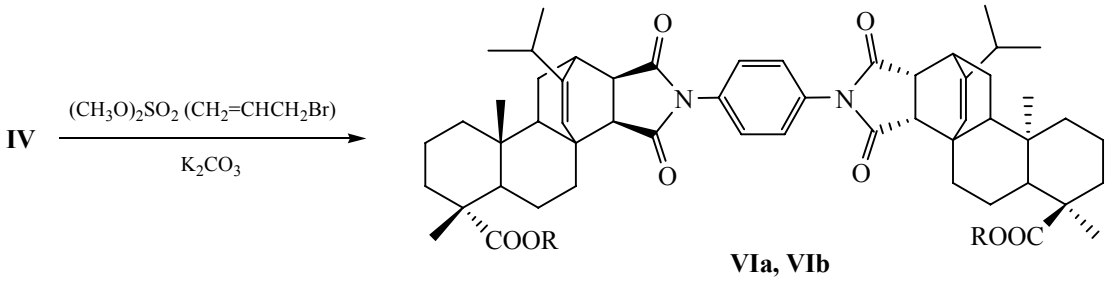
IR spectra of compounds **IIIa–IIIl** contained no absorption bands of C=O of anhydride group (1780 and 1840 cm^{-1}), and the bands of C=O stretching at 1690 and 1760 cm^{-1} appeared, characteristic of imide ring of maleopimaric acid [15]. Absorption bands at 1500 (C=C_{arom}) and 1390 cm^{-1} (C–N) were observed in the spectra as well. In the ^{1}H NMR spectra of the compounds, the signals characteristic of maleopimaric acid were retained [16], and the signals corresponding to the protons of *N*-aryl fragment (6.80–8.05 ppm) appeared. The mass spectra contained a peak of molecular ion $[M + 1]^+$.

Reaction of aminoimides **IIId** and **IIIe** with maleopimaric acid in solution and in melt was studied. It was found that the reaction of maleopimaric acid with *p*-aminoimide **IIId** (molar ratio of 1.5 : 1) in 1,2-dichlorobenzene under reflux during 3–8 h yielded diimide diacid **IV** in 44–47% yield; that acid has been earlier obtained from levopimaric acid and *N,N'*-(1,4-phenylene)dimaleimide [8]. The reaction of *p*-aminoimide **IIId** with maleopimaric acid in melt (molar ratio of 1 : 5) at 260–270°C during 2 h afforded the target product **IV** with yield of 37% [10] (Scheme 2).

The reaction of maleopimaric acid with *m*-aminoimide **IIIe** under the similar conditions resulted in a hardly separable mixture of diimide diacid **V** and unreacted starting compounds (^{1}H NMR).

Diimide diacids **IV** and **V** could be prepared in higher yield via reaction of maleopimaric acid with *p*- and *m*-phenylenediamines (molar ratio of 3 : 1) in 1,2-dichlorobenzene under reflux; the yield of diimide diacid **IV** achieved 68%, pure diacid **V** was isolated by preparative TLC in 48% yield. The higher yields of the target acids **IV** and **V** as compared to the reaction of maleopimaric acid with *p*- and *m*-aminoimides **IIId** and **IIIe** could be explained by possibility of the formation of oligomeric products from the starting aminoimides **IIId** and **IIIe** at 180–260°C [5, 6].

Scheme 3.



VIa, VIb

R = CH_3 (**a**), $CH_2CH{=}CH_2$ (**b**).

Treatment of diacid **IV** with dimethyl sulfate or allyl bromide in DMF in the presence of K_2CO_3 afforded dimethyl ester **VIa** and diallyl ester **VIb** in 92 and 78% yield, respectively (Scheme 3).

The prepared compounds **V**, **VIa**, and **VIb** were colorless crystalline substances soluble in DMF, DMSO, acetone, toluene, and chloroform; diacid **IV** was soluble in DMF and DMSO and poorly soluble in common organic solvents.

Composition and structure of compounds **IV–VI** were confirmed by elemental analysis, mass spectrometry, IR, ^{1}H, and ^{13}C NMR spectroscopy data. According to ^{1}H NMR, purity of the prepared compounds was of 98±1%. IR spectra of compounds **IV–VI** contained the characteristic absorption bands coinciding with the proposed compounds structure, cm^{-1}: 1770–1780 and 1710–1714 [(C=O)N], 1510−1514 ($C{=}C_{arom}$), and 1390–1370 (C–N). ^{1}H NMR spectra of the products contained the signals characteristic of acid **I** [16] and of *N*-aryl substituents at 6.81–7.53 ppm.

Thermal stability of imides **IIIa**, **IIId**, **IIIf**, **IIIh–IIIj**, and **IIIl** was determined by derivatography method [17]. The compounds were found to be thermally stable, and their decomposition occurred at 315–320°C (30–35°C above the decomposition point of the starting acid **I**). Thermal stability of *p*-iodophenylimide **IIIl** was the same as that of maleopimaric acid (decomposition point 290°C). Diimide diacid **IV** melted at 396–398°C with decomposition.

All the prepared compounds are of interest as potential high-temperature modifiers of industrial polymeric and elastomeric compositions. Aminoimides **IIId** and **IIIe**, diimide diacids **IV** and **V**, and esters **VIa–VIb** can be used in synthesis of new polyesterimide polymers and co-polymers.

EXPERIMENTAL

IR spectra were recorded with a Bruker Tensor 27 IR Fourier spectrometer (KBr pellets). ^{1}H and ^{13}C NMR spectra were registered with an AVANCE 500 instrument operating at 500 (^{1}H) or 125 (^{13}C) MHz (solutions in DMSO-d_6 in the cases of **IIIa–IIIl**, **IV**, **V**; or in $CDCl_3$ in the cases of **VIa–VIb**). Mass spectra were obtained with an Accela mass spectrometer equipped with an LCQ Fleet mass detector at atmospheric pressure chemical ionization (APCI) mode. Elemental analysis was performed with a VARIO Micro Cube CHNS-analyzer.

Thermal stability of the *N*-arylimides was studied with a NETZSCH STA 409 PC/PG derivatograph in argon at heating rate of 5 deg min^{-1}. In the case of diacid **IV**, a MOM Q-1500D derivatograph was used, other conditions being the same.

The starting rosin–maleic anhydride adduct was prepared by treatment of pine turpentine colophony (1000 g) with maleic anhydride (200 g) under argon at 180–200°C during 8 h. Content of maleopimaric acid was of 56.7% according to ^{1}H NMR; softening temperature was of 112–114°C, acid number reached 260 mg of KOH per g.

Maleopimaric acid *N*-arylimides (IIIa–IIIl) (*general procedure*). A mixture of 10 g of rosin–maleic anhydride adduct, 0.0175 mol of the aromatic amine, and 25 mL of toluene was heated under reflux with a condenser and Dean–Stark trap during 40 h and then incubated at 18–20°C during 48 h. The imide precipitate was filtered off, washed with toluene (3 × 5 mL), and dried in air.

Maleopimaric acid *N*-phenylimide (IIIa). Yield 5.09 g (75.6% with respect to maleopimaric acid), mp 305–307°C. Found, %: C 75.43; H 8.19; N 2.71. $C_{30}H_{37}NO_4$. Calculated, %: C 75.76; H 7.84; N 2.94.

Maleopimaric acid *N*-(*p*-methylphenyl)imide (IIIb). Yield 6.27 g (90.3%), mp 302–304°C. Found, %: C 76.21; H 7.79; N 2.68. $C_{31}H_{39}NO_4$. Calculated, %: C 76.04; H 8.03; N 2.86.

Maleopimaric acid *N*-(*p*-hydroxyphenyl)imide (IIIf). Yield 6.01 g (86.2%), mp 308–310°C. Found, %: C 73.09; H 7.44; N 2.93. $C_{30}H_{37}NO_5$. Calculated, %: C 73.29; H 7.59; N 2.85.

Maleopimaric acid *N*-(*p*-bromophenyl)imide (IIIk). Yield 6.74 g (85.7%), mp 275–277°C. Found, %: C 64.64; H 7.69; N 2.60. $C_{30}H_{36}BrNO_4$. Calculated, %: C 64.98; H 6.54; N 2.53.

The spectral parameters of imides **IIIa**, **IIIb**, **IIIf**, and **IIIk** coincided with those described in [10].

Maleopimaric acid *N*-(*o*-methylphenyl)imide (IIIc). Yield 5.28 g (76.0%), mp 279–281°C. IR spectrum, ν, cm^{-1}: 2570 (O–H), 1771, 1707 [(C=O)N], 1496 (C=C_{arom}), 1384 (C–N). ^{1}H NMR spectrum, δ, ppm (a mixture of two antropoisomers in a ratio of 1 : 0.74, the spectrum of the major one is given): 0.56 s (3H, $C^{20}H_3$), 0.90 m (1H), 0.94 d, 0.97 d [6H, $(C\underline{H}_3)_2CH$, *J* 7 Hz], 1.05 s (3H, $C^{18}H_3$), 1.17 m (2H), 1.35–1.75 m (10H), 1.93 s (3H, $C\underline{H}_3C_6H_4$), 2.17 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 7 Hz], 2.33 m (1H, C^7H_{eq}), 2.70 d (1H, $C^{15}H$, *J* 8 Hz), 3.00 br.s (1H, $C^{12}H$), 3.08 d.d (1H, $C^{16}H$, *J* 8, 2.5 Hz), 5.51 s (1H, $C^{14}H$), 7.05 d (1H, H_{arom}, *J* 7.5 Hz), 7.24–7.33 m (3H, H_{arom}). Mass spectrum, *m/z*: 491 $[M + 1]^+$. Found, %: C 75.72; H 7.89; N 2.90. $C_{31}H_{39}NO_4$. Calculated, %: C 76.04; H 8.03; N 2.86.

Maleopimaric acid *N*-(*p*-aminophenyl)imide (IIId). Yield 6.92 g (99.4%), mp 288–290°C. IR spectrum, ν, cm^{-1}: 2620 (O–H), 1768, 1695 [(C=O)N], 1496 (C=C_{arom}), 1390 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.91 d, 0.92 d [6H, $(C\underline{H}_3)_2CH$, *J* 6 Hz], 0.96 m (1H), 1.04 s (3H, $C^{18}H_3$), 1.15 m (2H), 1.36–1.57 m (7H), 1.61–1.71 m (3H), 2.14 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 6 Hz], 2.40 m (1H, C^7H_{eq}), 2.62 d (1H, $C^{15}H$, *J* 8 Hz), 2.93 br.s (1H, $C^{12}H$), 2.95 d.d (1H, $C^{16}H$, *J* 8, 3 Hz), 5.47 s (1H, $C^{14}H$), 6.53 d (2H, H_{arom}, *J* 9 Hz), 6.62 d (2H, H_{arom}, *J* 9 Hz). Mass spectrum, *m/z*: 491 $[M + 1]^+$. Found, %: C 72.44; H 7.60; N 5.38. $C_{30}H_{38}N_2O_4$. Calculated, %: C 73.44; H 7.81; N 5.93.

Maleopimaric acid *N*-(*m*-aminophenyl)imide (IIIe). Yield 6.12 g (87.9%), mp 349–351°C. IR spectrum, ν, cm^{-1}: 2620 (O–H), 1767, 1694 [(C=O)N], 1517 (C=C_{arom}), 1388 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.90 m (1H), 0.93 d [6H, $(C\underline{H}_3)_2CH$, *J* 7 Hz], 1.05 s (3H, $C^{18}H_3$), 1.15 m (2H), 1.35–1.72 m (10H), 2.15 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 7 Hz], 2.40 m (1H, C^7H_{eq}), 2.66 d (1H, $C^{15}H$, *J* 8 Hz), 2.94 br.s (1H, $C^{12}H$), 2.98 d.d (1H, $C^{16}H$, *J* 8, 3 Hz), 5.28 br.s (2H, NH_2), 5.48 s (1H, $C^{14}H$), 6.11 d (1H, H_{arom}, *J* 8 Hz), 6.20 s (1H, H_{arom}), 6.52 d (1H, H_{arom}, *J* 8 Hz), 7.03 m (1H, H_{arom}). Mass spectrum, *m/z*: 491 $[M + 1]^+$. Found, %: C 73.63; H 7.10; N 5.88. $C_{30}H_{38}N_2O_4$. Calculated, %: C 73.44; H 7.81; N 5.93.

Maleopimaric acid *N*-(*p*-methoxyphenyl)imide (IIIg). Yield 7.12 g (99.3%), mp 286–288°C. IR spectrum, ν, cm^{-1}: 2587 (O–H), 1769, 1701 [(C=O)N], 1512 (C=C_{arom}), 1399 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.91 d, 0.92 d [6H, $(C\underline{H}_3)_2CH$, *J* 7 Hz], 0.96 m (1H), 1.05 s (3H, $C^{18}H_3$), 1.16 m (2H), 1.30–1.74 m (10H), 2.15 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 7 Hz], 2.42 m (1H, C^7H_{eq}), 2.68 d (1H, $C^{15}H$, *J* 8 Hz), 2.95 br.s (1H, $C^{12}H$), 3.00 d.d (1H, $C^{16}H$, *J* 8, 2.5 Hz), 3.76 s (3H, CH_3O), 5.50 s (1H, $C^{14}H$), 6.97 m (4H, H_{arom}). Mass spectrum, *m/z*: 506 $[M + 1]^+$. Found, %: C 73.90; H 7.45; N 2.90. $C_{31}H_{39}NO_5$. Calculated, %: C 73.63; H 7.77; N 2.77.

Maleopimaric acid *N*-(*p*-fluorophenyl)imide (IIIh). Yield 5.52 g (78.8%), mp 306–308°C. IR spectrum, ν, cm^{-1}: 2579 (O–H), 1772, 1705 [(C=O)N], 1510 (C=C_{arom}), 1394 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.90 m (1H), 0.91 d, 0.92 d [6H, $(C\underline{H}_3)_2CH$, *J* 6 Hz], 1.05 s (3H, $C^{18}H_3$), 1.16 m (2H), 1.34–1.74 m (10H), 2.16 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 6 Hz], 2.42 m (1H, C^7H_{eq}), 2.71 d (1H, $C^{15}H$, *J* 8 Hz), 3.00 br.s (1H, $C^{12}H$), 3.03 d.d (1H, $C^{16}H$, *J* 8, 3 Hz), 5.51 s (1H, $C^{14}H$), 7.10 m (2H, H_{arom}), 7.30 m (2H, H_{arom}). Mass spectrum, *m/z*: 494 $[M + 1]^+$. Found, %: C 73.09; H 7.70; N 2.99. $C_{30}H_{36}FNO_4$. Calculated, %: C 73.00; H 7.35; N 2.84.

Maleopimaric acid *N*-(*p*-chlorophenyl)imide (IIIi). Yield 5.74 g (79.4%), mp 296–298°C. IR spectrum, ν, cm^{-1}: 2577 (O–H), 1773, 1706 [(C=O)N], 1493 (C=C_{arom}), 1390 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.90 m (1H), 0.91 d, 0.92 d [6H, $(C\underline{H}_3)_2CH$, *J* 6 Hz], 1.05 s (3H, $C^{18}H_3$), 1.16 m (2H), 1.32–1.74 m (10H), 2.15 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 6 Hz], 2.41 m (1H, C^7H_{eq}), 2.71 d (1H, $C^{15}H$, *J* Hz), 2.96 br.s (1H, $C^{12}H$), 3.03 d.d (1H, $C^{16}H$, *J* 8, 2.5 Hz), 5.51 s (1H, $C^{14}H$), 7.09 d (2H, H_{arom}, *J* 9 Hz), 7.53 d (2H, H_{arom}, *J* 9 Hz). Mass spectrum, *m/z*: 511 $[M + 1]^+$. Found, %: C 70.89; H 7.32; N 2.94. $C_{30}H_{36}ClNO_4$. Calculated, %: C 70.64; H 7.11; N 2.75.

Maleopimaric acid *N*-(*m*-chlorophenyl)imide (IIIj). Yield 5.89 g (81.5%), mp 273–275°C. IR spectrum, ν,

cm^{-1}: 2580 (O–H), 1774, 1708 [(C=O)N], 1478 (C=C_{arom}), 1382 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (3H, $C^{20}H_3$), 0.88 m (1H), 0.91 d, 0.92 d [6H, $(C\underline{H}_3)_2CH$, *J* 6 Hz], 1.05 s (3H, $C^{18}H_3$), 1.16 m (2H), 1.34–1.76 m (10H), 2.16 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 6 Hz], 2.42 m (1H, C^7H_{eq}), 2.71 d (1H, $C^{15}H$, *J* 7 Hz), 2.96 br.s (1H, $C^{12}H$), 3.04 d.d (1H, $C^{16}H$, *J* 8, 2.5 Hz), 5.52 s (1H, $C^{14}H$), 7.05 m (1H, H_{arom}), 7.15 m (1H, H_{arom}), 7.49 m (2H, H_{arom}). Mass spectrum, *m/z*: 511 $[M + 1]^+$. Found, %: C 70.38; H 7.29; N 2.89. $C_{30}H_{36}ClNO_4$. Calculated, %: C 70.64; H 7.11; N 2.75.

Maleopimaric acid *N*-(*p*-iodophenyl)imide (IIII). Yield 5.08 g (59.6%), mp 241–243°C. IR spectrum, ν, cm^{-1}: 2575 (O–H), 1773, 1704 [(C=O)N], 1488 (C=C_{arom}), 1390 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.55 s (3H, $C^{20}H_3$), 0.89 d and 0.91 d [6H, $(C\underline{H}_3)_2CH$, *J* 6 Hz], 0.91 m (1H), 1.04 s (3H, $C^{18}H_3$), 1.15 m (2H), 1.35–1.72 m (10H), 2.14 sextet [1H, $(CH_3)_2C\underline{H}$, *J* 6 Hz], 2.41 m (1H, C^7H_{eq}), 2.70 d (1H, $C^{15}H$, *J* 8 Hz), 2.95 br.s (1H, $C^{12}H$), 3.02 d.d (1H, $C^{16}H$, *J* 8, 3 Hz), 5.50 s (1H, $C^{14}H$), 6.87 d (2H, H_{arom}, *J* 8 Hz), 7.81 m (2H, H_{arom}, *J* 8 Hz). Mass spectrum, *m/z*: 602 $[M + 1]^+$. Found, %: C 59.64; H 6.11; N 3.04. $C_{30}H_{36}INO_4$. Calculated, %: C 59.90; H 6.03; N 2.33.

Diimide-diacid (IV). *a*. A solution of 0.7 g (0.0014 mol) of maleopimaric acid *N*-(4-aminophenyl)imide **IIId** and 0.85 g (0.0021 mol) of maleopimaric acid in 3 mL of 1,2-dichlorobenzene was refluxed during 3–8 h and then incubated at 18–20°C during 48 h. The precipitate was filtered off, washed with toluene (3 × 0.5 mL), and dried in air during 48 h. Yield 44% (3 h), 47% (8 h).

b. A solution of 3 g (0.0075 mol) of maleopimaric acid and 0.27 g (0.0025 mol) of *p*-phenylenediamine in 6 mL of 1,2-dichlorobenzene was refluxed during 8 h and then incubated during 48 h at 18–20°C. The precipitate was filtered off, washed with toluene (3 × 2 mL), and dried in air during 48 h. Yield 68% (1.49 g), mp 398–399°C (decomp.). IR spectrum, ν, cm^{-1}: 2550 (O–H), 1770, 1710 [(C=O)N], 1510 (C=C_{arom}), 1380 (C–N). Mass spectrum, *m/z*: 874 $[M + 1]^+$. Found, %: C 74.41; H 8.07; N 2.97. $C_{54}H_{68}N_2O_8$. Calculated, %: C 74.28; H 7.85; N 3.21. The spectral characteristics coincided with the reference data [8].

Diimide-diacid (V). A solution of 3 g (0.0075 mol) of maleopimaric acid and 0.27 g (0.0025 mol) of *m*-phenylenediamine in 6 mL of 1,2-dichlorobenzene was refluxed during 8 h. The solvent was removed under reduced pressure (10 mmHg), and 3.24 g of the product was obtained. The target diimide diacid **V** was isolated by preparative TLC on Fluka Silica plates (10 × 10 cm, eluent hexane–acetone, 1.1 : 1). 0.031 g (48%) of diacid **V** with mp 336–338°C was obtained from 0.1 g of the reaction product. IR spectrum, ν, cm^{-1}: 2550 (O–H), 1770, 1710 [(C=O)N], 1510 (C=C_{arom}), 1380 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.56 s (6H, $C^{20}H_3$), 0.90 d, 0.93 d [12H, $2(C\underline{H}_3)_2CH$, *J* 7 Hz], 1.05 s (6H, $2C^{18}H_3$), 1.18 m (4H), 1.36–1.72 m (20H), 2.38 sextet [2H, $2(CH_3)_2C\underline{H}$, *J* 7 Hz], 2.39 m (2H, $2C^7H_{eq}$), 2.71 d (2H, $2C^{15}H$, *J* 8 Hz), 2.95 br.s (2H, $2C^{12}H$), 3.03 d.d (2H, $2C^{16}H$, *J* 8, 3 Hz), 5.47 s (2H, $2C^{14}H$), 6.81 t (2H, H_{arom}, *J* 2 Hz), 7.11 d.d (4H, H_{arom}, *J* 8, 2 Hz), 7.53 t (2H, H_{arom}, *J* 8 Hz). Mass spectrum, *m/z*: 874 $[M + 1]^+$.

Diacid dimethyl ester (VIa). A mixture of 0.20 g (0.23 mmol) of diacid **IV**, 0.086 mL (0.92 mmol) of dimethylsulfate, and 0.12 g (0.92 mmol) of potassium carbonate in 2 mL of DMF was stirred during 14 h at 18–20°C. After the reaction was complete, the mixture was added into 70 mL of water upon vigorous stirring over 30 min and stirred during 1 h. The precipitate was filtered off, washed with water (2 × 5 mL), and dried in air. Yield 92% (0.19 g), mp 268–270°C. IR spectrum, ν, cm^{-1}: 1780, 1715 [(C=O)N], 1510 (C=C_{arom}), 1375 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.63 s (6H, $2C^{20}H_3$), 0.97 m (2H), 0.97 d and 0.99 d [12H, $2(C\underline{H}_3)_2CH$, *J* 7 Hz], 1.17 s (6H, $2C^{18}H_3$), 1.20–1.31 m (4H), 1.44–1.81 m (20H), 2.25 sextet [2H, $2(CH_3)_2C\underline{H}$, *J* 7 Hz], 2.55 m (2H, $2C^7H_{eq}$), 2.60 d (2H, $2C^{15}H$, *J* 8 Hz), 2.96 m (2H, $2C^{16}H$), 3.16 br.s (2H, $2C^{12}H$), 3.69 s (6H, $2OCH_3$), 5.50 s (2H, $2C^{14}H$), 7.22 s (4H, H_{arom}). Mass spectrum, *m/z*: 902 $[M + 1]^+$. Found, %: C 74.79; H 8.27; N 3.26. $C_{54}H_{68}N_2O_8$. Calculated, %: C 74.64; H 8.05; N 3.11.

Diacid diallyl ester (VIb) was prepared similarly from 0.20 g (0.23 mmol) of diacid **IV**, 0.058 mL (0.69 mmol) of allyl bromide, and 0.095 g (0.69 mmol) of potassium carbonate. Yield 78% (0.17 g), mp 165–167°C. IR spectrum, ν, cm^{-1}: 1774, 1714 [(C=O)N], 1514 (C=C_{arom}), 1367 (C–N). ^{1}H NMR spectrum, δ, ppm: 0.63 s (6H, $C^{20}H_3$), 0.96 m (2H), 0.97 d and 0.99 d [12H, $2(C\underline{H}_3)_2CH$, *J* 7 Hz], 1.19 s (6H, $2C^{18}H_3$), 1.24–1.31 m (4H), 1.43–1.83 m (20H), 2.50 sextet [2H, $2(CH_3)_2C\underline{H}$], 2.56 m (2H, $2C^7H_{eq}$), 2.60 d (2H, $2C^{15}H$, *J* 8 Hz), 2.96 m (2H, $2C^{16}H$), 3.16 br.s (2H, $2C^{12}H$), 4.59 m (4H, $2OCH_2$), 5.23 d (2H, $=CH_2$, 2H-*trans*, *J* 10 Hz), 5.33 d (2H, $=CH_2$, 2H-*cis*, *J* 17 Hz), 5.50 s (2H, $2C^{14}H$), 5.93 m (2H, $2C\underline{H}=CH_2$), 7.22 s (4H, H_{arom}). Mass spectrum, *m/z*: 954 $[M + 1]^+$. Found,

%: C 75.81; H 8.23; N 2.76. $C_{60}H_{76}N_2O_8$. Calculated, %: C 75.60; H 8.04; N 2.94.

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