

Synthesis, Physicochemical Properties, and Thermo-Oxidative Stability of Diesters of 5,7-Dimethyl-1,3-Adamantanediol and 5,7-Dimethyl-1,3-bis(Hydroxymethyl)adamantane

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Received January 22, 2018

Abstract—A series of diesters on the basis of 5,7-dimethyl-1,3-adamantanediol and 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane and C₃–C₁₀ aliphatic acids have been synthesized and their physicochemical and thermo-oxidative properties have been studied. The properties of the esters obtained have been compared to those of trimethylolpropane and neopentyl glycol esters.

Keywords: esters, thermo-oxidative stability, adamantanediol, thermally stable oils

DOI: 10.1134/S096554411808008X

This work is devoted to studying the physicochemical properties and thermo-oxidative stability of esters obtained from dihydroxy derivatives of adamantane, namely, 5,7-dimethyl-1,3-adamantanediol and 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane, and linear C₃–C₁₀ aliphatic acids. The choice of these objects of study is due to the following several aspects:

—uniqueness of the geometrical structure of cage compounds, which have been the object of continuous studies for several decades [1];

—a set of specialty performance characteristics [2–5];

—practical significance of functional derivatives of adamantane [6–8].

Currently, esters obtained from neoalkyl polyols (neopentyl glycol, trimethylolpropane, and trimethylololthane) are widely used as the base of synthetic materials in addition to esters of dicarboxylic acids. Such esters have quite high thermo-oxidative stability and good low-temperature properties, which determine their use as basestock or components of synthetic lubricants [9–21] and reactants in the synthesis of macromolecules with valuable practical properties [22–27].

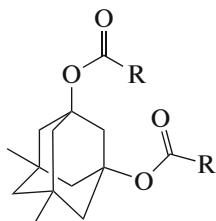
Diesters of alkyladamantanols are proposed as additives that increase the oxidative stability and viscosity of lubricating oils and transmission fluids [28,

29], power fluids in gas turbine units [30], and electrical insulating oils [31].

In continuation of the works [2–5, 28, 29], in which the thermo-oxidative stability and antiwear ability of diesters had been studied, a number of diesters on the basis of 5,7-dimethyl-1,3-adamantanediol and 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane and linear aliphatic acids were synthesized and their physicochemical and thermo-oxidative properties were examined in this work. The two series of esters differ in the position of the ester groups relative to the adamantane cage. The choice of the length of the aliphatic acid residue was determined by the aim to make final diesters similar in molecular weight and viscosity—temperature and physicochemical characteristics to di- and triesters of neopentyl glycol (NPG) and trimethylolpropane (TMP), in particular, NPG dicaprylate/dicaprate and TMP tricaprylate/tricaprate, which are being widely used in industry and medicine at present. The methyl groups in the bridgehead positions of the adamantane cage in the reactant molecules lead to improvement of the physicochemical characteristics (thermo-oxidative stability, pour point, and kinematic viscosity) of the resulting esters in comparison with the unsubstituted analogues [3].

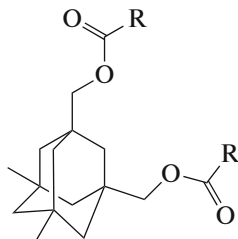
EXPERIMENTAL

The authors synthesized and studied two series of esters. The esters from 5,7-dimethyl-1,3-adamantane-1,3-diol (I)–(VI) were synthesized by esterification of the corresponding acids in the presence of a homogeneous catalyst (trifluoromethanesulfonic acid). The yields of esters I–VI after purification by vacuum distillation were 46–88%:



R = C₂H₅ (I), C₃H₇ (II), C₄H₉ (III), C₇H₁₅ (IV), C₈H₁₇ (V), C₉H₁₉ (VI).

Esters (VII)–(X) were obtained via the acylation of 5,7-dimethyl-1,3-bis(carboxymethyl)adamantane with the chlorides of the corresponding acids in the presence of triethylamine. Esters (VII)–(X) were obtained with yields of 57–80% after purification by vacuum distillation:



R = C₆H₁₃ (VII), C₇H₁₅ (VIII), C₈H₁₇ (IX), C₉H₁₉ (X).

5,7-Dimethyladamantane-1,3-diol was obtained according to the procedure [32]. Yield 61%, mp 217–218°C (lit. mp 217–218°C). Assay 98.5%.

5,7-Dimethyl-1,3-bis(hydroxymethyl)adamantane was obtained according to the procedure [29]. Yield 73%, mp 264–265°C (lit. mp 270°C). Assay 99.0%.

5,7-Dimethyladamantane-1,3-diyl dipropionate I. A mixture of 35 g (0.179 mol) of 5,7-dimethyladamantane-1,3-diol, 30 g (0.405 mol, 30.5 mL) of propionic acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether was refluxed with a Dean–Stark trap for 10 h. The reaction mixture was diluted with 100 mL of toluene, washed three times with a 5% aqueous solution of KOH followed by water to a neutral medium, and dried over sodium sulfate. The solvent was evaporated, and the residue was passed through a bed of silica gel (module 1) saturated with triethylamine and eluted with toluene. The solvent was evaporated, and the residue containing the product was distilled in vacuum. A fraction with bp 110–116°C (0.020 Torr) was collected during the distillation. The weight of the product after the distillation was 39.2 g. The yield 71%, $n_D^{20} = 1.4778$.

IR spectrum, ν , cm⁻¹: 1735 (C=O). ¹H NMR spectrum, δ , ppm: 0.92 (s, 6H, CH₃), 1.05 (t, $J = 7.36$ Hz, 6H, CH₃), 1.12 (s, 2H, CH₂Ad), 1.71–1.78 (m, 8H, CH₂Ad), 2.17–2.22 (m, 4H, CH₂), 2.32 (s, 2H, CH₂Ad). ¹³C NMR spectrum, δ , ppm: 9.2 (CH₃), 28.8 (CH), 29.1 (CH₃), 34.7 (C), 43.8 (CH₂), 46.2 (CH₂), 49.5 (CH₂), 50.4 (CH₂), 81.2 (C), 173.7 (C). Mass spectrum, m/z (I_{rel} , %): 234 (36), 216 (20), 177 (100), 161 (50), 160 (40), 145 (28), 120 (56), 105 (34), 57 (88). Found, %: C 70.13; H 9.12. Calculated for C₁₈H₂₈O₄, %: C 70.10; H 9.15.

5,7-Dimethyladamantane-1,3-diyl dibutanoate II was obtained similarly to diester I from 23 g (0.117 mol) of 5,7-dimethyladamantane-1,3-diol, 23 g (0.261 mol, 24 mL) of butyric acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether. The weight of the product after the distillation was 31.4 g. The yield 80%, bp 120–126°C (0.020 Torr), $n_D^{20} = 1.4745$. IR spectrum, ν , cm⁻¹: 1732 (C=O). ¹H NMR spectrum, δ , ppm: 0.87–0.91 (m, 12H, CH₃), 1.12 (s, 2H, CH₂Ad), 1.51–1.60 (m, 4H, CH₂), 1.75 (s, 8H, CH₂Ad), 2.13–2.17 (m, 4H, CH₂), 2.31 (s, 2H, CH₂Ad). ¹³C NMR spectrum, δ , ppm: 13.7 (CH₃), 18.6 (CH₂), 29.1 (CH₃), 34.7 (C), 37.5 (CH₂), 43.9 (CH₂), 46.2 (CH₂), 49.5 (CH₂), 81.2 (C), 172.9 (C). Mass spectrum, m/z (I_{rel} , %): 248 (60), 230 (18), 151 (100), 161 (58), 160 (42), 145 (16), 120 (36), 71 (26), 43 (20). Found, %: C 71.43; H 9.57. Calculated for C₂₀H₃₂O₄, %: C 71.39; H 9.59.

5,7-Dimethyladamantane-1,3-diyl dipentanoate III was obtained similarly to diester I from 22 g (0.112 mol) of 5,7-dimethyladamantane-1,3-diol, 25 g (0.245 mol, 27 mL) of valeric acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether. The weight of the product after the distillation was 36 g. The yield 88%, bp 140–146°C (0.027 Torr), $n_D^{20} = 1.4742$. IR spectrum, ν , cm⁻¹: 1732 (C=O). ¹H NMR spectrum, δ , ppm: 0.84–0.92 (m, 12H, CH₃), 1.12 (s, 2H, CH₂Ad), 1.25–1.34 (m, 4H, CH₂), 1.48–1.55 (m, 4H, CH₂), 1.75 (s, 8H, CH₂Ad), 2.14–2.19 (m, 4H, CH₂), 2.31 (s, 2H, CH₂Ad). ¹³C NMR spectrum, δ , ppm: 13.7 (CH₃), 22.3 (CH₂), 27.3 (CH₂), 29.1 (CH₃), 34.7 (C), 35.4 (CH₂), 43.9 (CH₂), 46.2 (CH₂), 49.5 (CH₂), 81.2 (C), 173.1 (C). Mass spectrum, m/z (I_{rel} , %): 262 (60), 244 (18), 205 (100), 161 (60), 120 (34), 105 (16), 85 (40), 57 (20). Found, %: C 72.52; H 9.93. Calculated for C₂₂H₃₆O₄, %: C 72.49; H 9.95.

5,7-Dimethyladamantane-1,3-diyl dioctanoate IV was obtained similarly to diester I from 27.44 g (0.14 mol) of 5,7-dimethyladamantane-1,3-diol, 40.32 g (0.28 mol) of caprylic acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether. The weight of the product after the distillation was 36 g. The yield 88%, bp

140–146°C (0.027 Torr), $n_D^{20} = 1.4745$. IR spectrum, ν , cm^{-1} : 1732 (C=O). ^1H NMR spectrum, δ , ppm: 0.82–0.85 (m, 6H, CH_3), 0.90–0.92 (m, 6H, CH_3), 1.12 (s, 2H, CH_2Ad), 1.18–1.24 (m, 16H, CH_2), 1.51–1.53 (m, 4H, CH_2), 1.73–1.74 (m, 8H, CH_2Ad), 2.13–2.18 (m, 4H, CH_2), 2.31 (s, 2H, CH_2Ad). ^{13}C NMR spectrum, δ , ppm: 14.2 (CH_3), 22.7 (CH_2), 25.1 (CH_2), 29.0 (CH_2), 29.1 (CH_3), 31.7 (CH_2), 34.7 (C), 35.6 (CH_2), 43.9 (CH_2), 46.2 (CH_2), 49.5 (CH_2), 81.2 (C), 173.1 (C). Mass spectrum, m/z (I_{rel} , %): 304 (38), 285 (16), 247 (98), 179 (20), 161 (98), 120 (60), 106 (30), 57 (100), 43 (48). Found, %: C 74.94; H 10.80. Calculated for $\text{C}_{28}\text{H}_{48}\text{O}_4$, %: C 74.95; H 10.78.

5,7-Dimethyladamantane-1,3-diyl dinonanoate V was obtained similarly to diester I from 20 g (0.102 mol) of 5,7-dimethyladamantane-1,3-diol, 48 g (0.30 mol) of pelargonic acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether. The weight of the product after the distillation was 22.4 g. The yield 46%, bp 195–197°C (0.032 Torr), $n_D^{20} = 1.4748$. IR spectrum, ν , cm^{-1} : 1732 (C=O). ^1H NMR spectrum, δ , ppm: 0.86 (t, $J = 6.64$ Hz, 6H, CH_3), 0.93 (s, 6H, CH_3), 1.14 (s, 2H, CH_2Ad), 1.22–1.30 (m, 20H, CH_2 , CH_2Ad), 1.50–1.57 (m, 4H, CH_2), 1.76 (s, 8H, CH_2), 2.18 (t, $J = 7.32$ Hz, 4H, CH_2), 2.32 (s, 2H, CH_2). ^{13}C NMR spectrum, δ , ppm: 14.2 (CH_3), 22.7 (CH_2), 25.2 (CH_2), 29.1 (CH_3), 29.2 (CH_2), 29.20 (CH_2), 29.3 (CH_2), 31.9 (CH_2), 34.8 (C), 35.7 (CH_2), 44.0 (CH_2), 46.2 (CH_2), 49.5 (CH_2), 81.2 (C), 173.1 (C). Mass spectrum, m/z (I_{rel} , %): 475 [$\text{M}-1$]⁺ (<2), 318 (66), 261 (100), 161 (70), 141 (23), 120 (26), 57 (30). Found, %: C 75.57; H 10.96. Calculated for $\text{C}_{30}\text{H}_{52}\text{O}_4$, %: C 75.58; H 10.99.

5,7-Dimethyladamantane-1,3-diyl didecanoate VI was obtained similarly to diester I from 20 g (0.102 mol) of 5,7-dimethyladamantane-1,3-diol, 52.7 g (0.31 mol) of capric acid, and 0.85 g (0.005 mol, 0.5 mL) of trifluoromethanesulfonic acid in 200 mL of petroleum ether. The weight of the product after the distillation was 23 g. The yield 46%, bp 205–206°C (0.035 Torr), $n_D^{20} = 1.4750$. IR spectrum, ν , cm^{-1} : 1732 (C=O). ^1H NMR spectrum, δ , ppm: 0.86 (t, $J = 7.32$ Hz, 6H, CH_3), 0.93 (s, 6H, CH_3), 1.14 (s, 2H, CH_2Ad), 1.20–1.33 (m, 26H, CH_2 , CH_2Ad), 1.50–1.58 (m, 4H, CH_2), 1.76 (s, 6H, CH_2Ad), 2.18 (t, $J = 7.32$ Hz, 4H, CH_2), 2.32 (s, 2H, CH_2Ad). ^{13}C NMR spectrum, δ , ppm: 14.2 (CH_3), 22.8 (CH_2), 25.1 (CH_2), 29.1 (CH_3), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 34.7 (C), 35.7 (CH_2), 44.0 (CH_2), 46.2 (CH_2), 49.5 (CH_2), 81.2 (C), 173.1 (C). Mass spectrum, m/z (I_{rel} , %): 332 (67), 275 (100), 161 (98), 120 (30), 57 (24),

43 (30). Found, %: C 76.14; H 11.16. Calculated for $\text{C}_{32}\text{H}_{56}\text{O}_4$, %: C 76.14; H 11.18.

(5,7-Dimethyladamantane-1,3-diyl)dimethanediyl diheptanoate VII. 45 g (50 mL, 0.346 mol) of enanthic acid was slowly added dropwise to 124 g (75 mL, 1.042 mol) of thionyl chloride upon reflux. The obtained mixture was heated upon reflux for 30 min, and the excess thionyl chloride was evaporated in vacuum. About 50 g of enanthoyl chloride was obtained as a yellow oil. 25 g (0.102 mol) of 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane, 70 mL of triethylamine, 50 g (0.337 mol) of enanthoyl chloride, and 200 mL of toluene are placed into a three-neck flask equipped with a mechanical stirrer and a reflux condenser. The obtained mixture is heated upon reflux for 3 h. The formed precipitate of triethylamine hydrochloride is filtered off, and the filtrate is evaporated in vacuum on a rotary evaporator. The residue is purified via vacuum distillation collecting a fraction with bp 200–202°C (0.036 Torr). The weight 37 g, yield 74%, $n_D^{20} = 1.4750$. IR spectrum, ν , cm^{-1} : 1739 (C=O). ^1H NMR spectrum, δ , ppm: 0.81–0.85 (m, 12H, CH_3), 1.06–1.09 (m, 10H, CH_2Ad , CH_2), 1.21–1.29 (m, 16H, CH_2Ad , CH_2), 2.26 (t, $J = 7.32$ Hz, 4H, CH_2), 3.67–3.69 (m, 4H, CH_2). ^{13}C NMR spectrum, δ , ppm: 14.1 (CH_3), 22.6 (CH_2), 25.0 (CH_2), 28.9 (CH_2), 30.1 (CH_3), 31.2 (C), 31.5 (CH_2), 34.4 (CH_2), 35.5 (C), 39.9 (CH_2), 45.1 (CH_2), 50.7 (CH_2), 72.9 (CH_2), 173.9 (C). Mass spectrum, m/z (I_{rel} , %): 304 (42), 285 (18), 247 (98), 179 (20), 161 (98), 120 (58), 105 (32), 57 (100), 43 (48). Found, %: C 74.98; H 10.75. Calculated for $\text{C}_{28}\text{H}_{48}\text{O}_4$, %: C 74.95; H 10.78.

(5,7-Dimethyladamantane-1,3-diyl)dimethanediyl dioctanoate VIII was obtained similarly to diester VII from 30 g (0.134 mol) of 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane, 70 mL of triethylamine, 55 g (0.338 mol) of capryloyl chloride, and 200 mL of toluene. The weight of the product after the distillation was 51 g. The yield 80%, bp 206–208°C (0.036 Torr), $n_D^{20} = 1.4748$. IR spectrum, ν , cm^{-1} : 1739 (C=O). ^1H NMR spectrum, δ , ppm: 0.81–0.84 (m, 12H, CH_3), 1.08–1.12 (m, 12H, CH_2Ad , CH_2), 1.21–1.25 (m, 16H, CH_2Ad , CH_2), 1.54–1.58 (m, 4H, CH_2), 2.25 (t, $J = 7.36$ Hz, 4H, CH_2), 3.67–3.68 (m, 4H, CH_2). ^{13}C NMR spectrum, δ , ppm: 14.1 (CH_3), 22.7 (CH_2), 25.1 (CH_2), 29.00 (CH_2), 29.2 (CH_2), 30.1 (CH_3), 31.2 (C), 31.8 (CH_2), 34.3 (CH_2), 35.5 (C), 39.9 (CH_2), 45.4 (CH_2), 50.7 (CH_2), 72.9 (CH_2), 173.9 (C). Mass spectrum, m/z (I_{rel} , %): 477 [$\text{M}^+ + 1$] (<1), 377 (18), 319 (38), 188 (52), 175 (100), 133 (42), 119 (86), 105 (30), 57 (60), 43 (24). Found, %: C 75.60; H 10.97. Calculated for $\text{C}_{30}\text{H}_{52}\text{O}_4$, %: C 75.58; H 10.99.

(5,7-Dimethyladamantane-1,3-diyl)dimethanediyl dinonanoate IX was obtained similarly to diester VII from 25 g (0.112 mol) of 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane, 36 mL of triethylamine, 45 g (0.255 mol) of pelargonoyl chloride, and 250 mL of toluene. The weight of the product after the distillation was 32 g. The yield 57%, bp 205–207°C (0.019 Torr), $n_D^{20} = 1.4752$. IR spectrum, ν , cm^{-1} : 1739 (C=O). ^1H NMR spectrum, δ , ppm: 0.85–0.87 (m, 12H, CH_3), 1.10–1.17 (m, 12H, CH_2Ad , CH_2), 1.25–1.28 (m, 22H, CH_2Ad , CH_2), 1.57–1.62 (m, 4H, CH_2), 2.30 (t, $J = 7.36$ Hz, 4H, CH_2), 3.72 (s, 4H, CH_2). ^{13}C NMR spectrum, δ , ppm: 14.2 (CH_3), 22.7 (CH_2), 25.1 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.3 (CH_2), 30.2 (CH_3), 31.3 (C), 31.9 (CH_2), 34.4 (CH_2), 35.5 (C), 39.9 (CH_2), 45.2 (CH_2), 50.7 (CH_2), 72.9 (CH_2), 174.1 (C). Mass spectrum, m/z (I_{rel} , %): 505 [M^+] (8), 406 (12), 333 (14), 188 (18), 175 (50), 141 (100), 119 (48), 105 (32), 57 (61), 43 (73). Found, %: C 76.13; H 11.15. Calculated for $\text{C}_{32}\text{H}_{56}\text{O}_4$, %: C 76.14; H 11.18.

(5,7-Dimethyladamantane-1,3-diyl)dimethanediyl didecanoate X was obtained similarly to diester VII from 25 g (0.112 mol) of 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane, 40 mL of triethylamine, 50 g (0.242 mol) of caproyl chloride, and 300 mL of toluene. The weight of the product after the distillation was 38 g. The yield 64%, bp 219–220°C (0.024 Torr), $n_D^{20} = 1.4750$. IR spectrum, ν , cm^{-1} : 1739 (C=O). ^1H NMR spectrum, δ , ppm: 0.84–0.86 (m, 12H, CH_3), 1.10–1.17 (m, 12H, CH_2Ad , CH_2), 1.25–1.28 (m, 24H, CH_2Ad , CH_2), 1.57–1.62 (m, 4H, CH_2), 2.30 (t, $J = 7.32$ Hz, 4H, CH_2), 3.72 (s, 4H, CH_2). ^{13}C NMR spectrum, δ , ppm: 14.2 (CH_3), 22.7 (CH_2), 25.1 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 30.2 (CH_3), 31.3 (C), 31.9 (CH_2), 34.4 (CH_2), 35.5 (C), 39.9 (CH_2), 45.2 (CH_2), 50.7 (CH_2), 72.9 (CH_2), 174.1 (C). Mass spectrum, m/z (I_{rel} , %): 534 [$\text{M}^+ + 1$] (10), 505 (16), 420 (34), 188 (52), 175 (34), 133 (42), 155 (90), 119 (38), 57 (65), 43 (100). Found, %: C 76.61; H 11.33. Calculated for $\text{C}_{34}\text{H}_{60}\text{O}_4$, %: C 76.64; H 11.35.

The qualitative characteristics and structures of the synthesized compounds were confirmed using state-of-the-art chromatographic and spectral methods (GC–MS, elemental analysis, and IR and NMR spectroscopy). The mass spectra were obtained on a ThermoFinnigan DSQ instrument using a BPX-5 30×0.32 capillary column at an ionizing electron energy of 70 eV. The elemental analysis was performed on a EuroVector 3000 EA elemental analyzer using L-cystine as the standard. IR spectra were recorded using a Shimadzu IRAffinity-1 spectrometer with an ATR accessory. ^1H and ^{13}C NMR spectra were recorded on

a Jeol JNM ECX-400 spectrometer (the operating frequency of 400 MHz) in CDCl_3 .

The physicochemical properties of the synthesized diesters were studied using conventional GOST and ASTM procedures (kinematic viscosity at positive and negative temperatures according to ASTM D7042, viscosity index according to GOST 25371, density at 20°C according to ASTM D7042, open cup flash point according to GOST 4333, and pour point according to GOST 20287).

The thermo-oxidative stability of the samples in a thin layer was studied by high-pressure differential scanning calorimetry (HP-DSC) according to ASTM E2009 (test method B) in aluminum crucibles in an oxygen atmosphere (35 atm, a flow rate of 50 mL/min) and in the dynamic mode (from 70 to 300°C at a rate of 10°C/min) using a DSC 204 HP Phoenix instrument (NETZSCH-Gerätebau GmbH, Germany).

The test results obtained for the samples of commercial esters of neopentyl polyols, namely, NPG dicaprylate/dicaprate (trade name is Waglinol 2/10480) and TMP tricaprylate/tricaprate (trade name is Waglinol 3/13480) (IQL) were used for comparison.

RESULTS AND DISCUSSION

The data on the physicochemical properties (kinematic viscosity at positive and negative temperatures, viscosity index, pour point, flash point, and density) and thermo-oxidative stability according to ASTM E2009 of compounds I–X and TMP and NPG esters are presented in Table 1.

Unlike lubricating properties, which improve with the growth of the hydrocarbon chain [28], the thermo-oxidative properties of adamantane-containing esters are tightly associated with their structure. It is seen from the obtained data that except for ester I, the other esters have good pour points below -40°C . The other parameters are seen to depend on the ester structure, namely, the position of the ester group relative to the adamantane cage. Thus, esters I–VI have higher viscosity at positive and negative temperatures and a lower viscosity index (VI) than esters VII–X. Less sterically hindered TMP and NPG esters have lower levels of viscosity at positive and especially negative temperatures and higher VIs.

Figures 1 and 2 present the results of the studies of the thermo-oxidative stability of esters (the ability of compounds to resist oxidation without antioxidant additives) according to ASTM E2009 in the form of oxidation onset temperature (OOT). It is seen from the presented data that the NPG ester is the least stable at high temperatures, thus, violent oxidation accompanied by a flash occurred during its test at 214°C . Esters I–VI, in which the ester group is directly bound to the adamantane cage, possess higher values of

Table 1. Physicochemical properties of 5,7-dimethyl-1,3-adamantanediol esters I–VI, 5,7-dimethyl-1,3-bis(hydroxymethyl)adamantane esters VII–X, and NPG and TMP esters

Sample No.	I	II	III	IV	V	VI	VII	VIII	IX	X	TMP tricaprylate/ tricaprate	NPG dicaprylate/ dicaprate
R =	–C ₂ H ₅	–C ₃ H ₇	–C ₄ H ₉	–C ₇ H ₁₅	–C ₈ H ₁₇	–C ₉ H ₁₉	–C ₆ H ₁₃	–C ₇ H ₁₅	–C ₈ H ₁₇	–C ₉ H ₁₉	–C ₇ H ₁₅ , –C ₉ H ₁₉	–C ₇ H ₁₅ , –C ₉ H ₁₉
Empirical formula	C ₁₈ H ₂₈ O ₄	C ₂₀ H ₃₂ O ₄	C ₂₂ H ₃₆ O ₄	C ₂₈ H ₄₈ O ₄	C ₃₀ H ₅₂ O ₄	C ₃₂ H ₅₆ O ₄	C ₂₈ H ₄₈ O ₄	C ₃₀ H ₅₂ O ₄	C ₃₂ H ₅₆ O ₄	C ₃₄ H ₆₀ O ₄	Mixture	Mixture
Molecular weight, g/mol	308.41	336.47	364.52	448.68	476.73	504.78	448.68	476.73	504.78	532.84	524–584	364–416
Kinematic viscosity, mm ² /s:												
at 100°C	3.98	4.22	4.94	7.15	7.57	7.28	5.77	6.16	6.44	7.13	4.39	2.51
at 40°C	44.41	35.64	34.80	50.59	70.19	52.78	32.08	38.46	43.38	48.17	19.49	8.30
at –30°C	–	26 046	12 595	30 718	33 194	20 338	8225	10 536	13 709	13 195	1332	273.0
at –40°C	–	> 100000	> 100000	75 225	> 100000	> 100000	38 512	50 506	68 076	> 100000	3989	690.3
Viscosity index	–4	22	62	99	57	96	123	106	97	106	139	137
Pour point, °C	–26	–48	–40	–46	–52	–50	–44	–46	–48	–40	–45	–54
Flash point, °C	194	190	204	232	250	258	226	238	252	262	256	210
Density at 20°C, kg/m ³	1067	1033	1018	979	966	946	983	976	968	956	942	914
Thermo-oxidative stability according to ASTM E2009, OOT, °C	242.5	241.7	234.2	224.9	197.9	191.6	212.90	214.96	216.34	210.25	215.8	214.1 with a flash

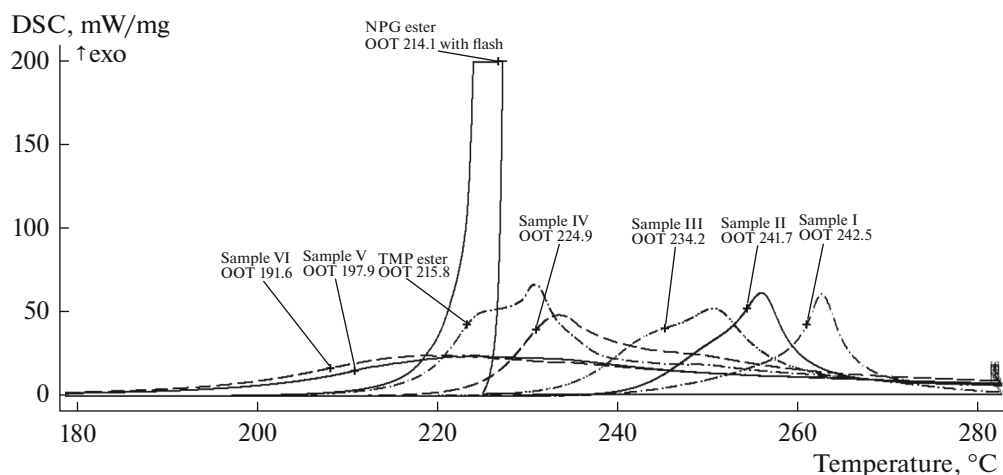


Fig. 1. Thermo-oxidative stability according to ASTM E2009 of 5,7-dimethyl-1,3-adamantanediol diesters I–VI and esters of neopentyl polyols.

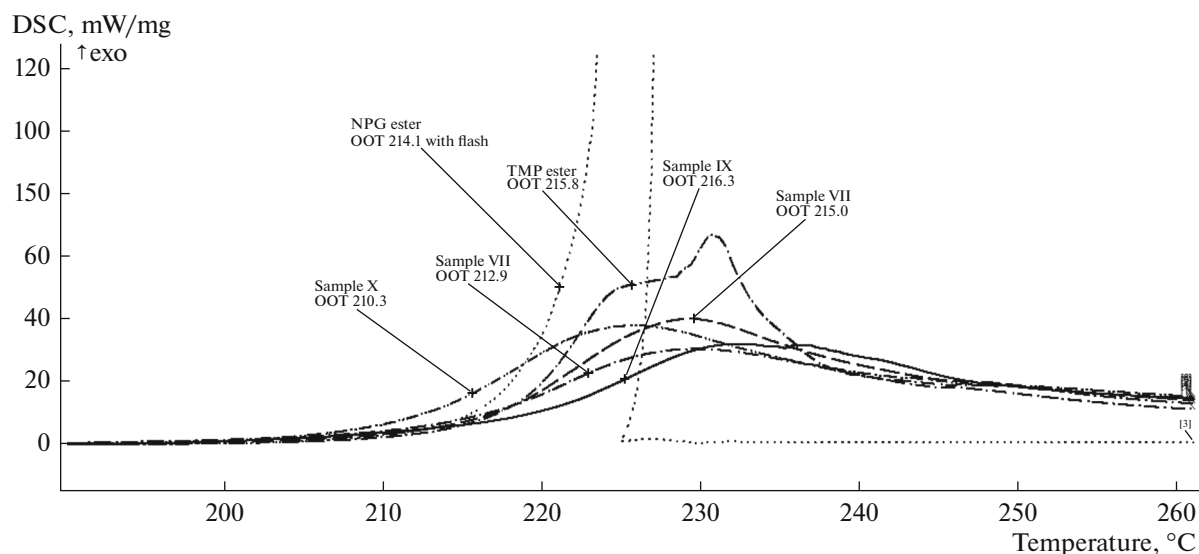


Fig. 2. Thermo-oxidative stability according to ASTM E2009 of 5,7-dimethyl-1,3-bis(carboxymethyl)adamantane diesters VII–X and esters of neopentyl polyols.

thermo-oxidative stability (OOT of 224.9–242.5°C), with the OOT value gradually decreasing with the growth in the hydrocarbon radical length from C₂ to C₇. Esters V and VI somewhat fall outside this series, apparently, because of degradation that could have occurred during their distillation, which is confirmed to some extent by the lower yields of these esters. Similar esters VII–X and the TMP ester have quite close values OOT (210–215°C); however, the oxidation intensity of 30 mW/mg for the adamantane series esters was about twofold below that of 50–60 mW/mg for the TMP ester.

CONCLUSIONS

The effect of the length of the hydrocarbon residue and structure of esters of dihydroxy derivatives of adamantane on the physicochemical and thermo-oxidative properties has been investigated. The adamantane-containing esters have been compared to commercial products, namely, neopentyl glycol dicaprylate/dicaprate and tricaprylate/tricaprate of trimethylolpropane. It has been shown the esters of dihydroxy derivatives of adamantane, in particular, more stable esters I–IV, can be in principle used as basestock for lubricating materials.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation, agreement no. 14.577.21.0237 (unique project identifier RFMEFI57716X0237), using the scientific equipment of the Study of Physicochemical Properties of Substances and Materials Center for Collective Use.

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Translated by E. Boltukhina