Skeletal rearrangement in the Ritter reaction of turpentine: A novel synthesis of *p*-menthane diamides

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A novel skeletal rearrangement in the Ritter reaction was examined which conveniently generated *p*-menthane diamides from turpentine. A probable reaction mechanism was proposed based on employing thermodynamic analysis. All the products were purified and characterised by ^{1}H NMR, IR, X-ray crystallography and ESI$^+$-MS.

Keywords: Ritter reaction, skeleton rearrangement, synthesis, *p*-menthane diamides

Amide functional groups are fundamental chemical building blocks in nature.[1–3] Amide compounds exhibit a wide range of biological activities and have been studied extensively in biology, medicine as well as in pesticides.[4–6] The Ritter reaction is a classical synthetic method which is used to prepare amides.[7,8] Many highly valuable pharmaceutical intermediates and heterocycles can be prepared conveniently from nitriles, alcohols, alkenes and tertiary halides by this procedure.[7–9] Over the last few decades, significant progress with catalysed Ritter reactions has been achieved.[10,11] In this reaction, an acid-catalysed nucleophilic addition of a nitrile to a carbenium ion, followed by hydrolysis generates an amide. Molecular rearrangements may occur if the intermediate carbonium ions isomerise to more stable structures.[7–12] However, to the best of our knowledge, there are few reports concerning the synthesis of amides *via* Ritter reactions.[7,11]

In continuation of our previous work on *p*-menthane derivatives synthesised from turpentine *via* a cationic resin-catalysed hydration reaction,[13] we envisioned a novel skeletal rearrangement Ritter reaction. This novel procedure offers a convenient approach to the synthesis of *p*-menthane diamides (Scheme 1).

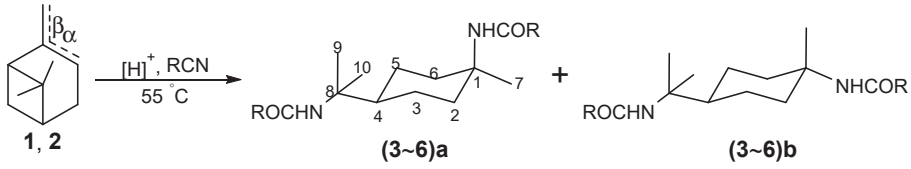
It has been reported that monoterpene derivatives with the *p*-menthane skeleton are useful compounds with a high bioactivity.[14] *p*-Menthane diamides **3a–4b** have been successfully synthesised by Kovals'skaya and coworkers.[15] However, attempts to synthesise analogues of these compounds from terpenes and terpineols were unsuccessful. Our investigation provides a robust approach for the preparation and utilisation of *p*-menthane diamides **3a–6b**.

In the initial screening, the reaction between turpentine and acetonitrile was chosen as the starting point for product characterisation and reaction optimisation. In a similar reaction to that of terpin hydrate with nitriles, the interaction of turpentine and acetonitrile also led to the formation of isomeric mixtures in a ratio of 3.7:1. However, in contrast to the work reported by Kovals'skaya and coworkers, these two isomers were shown to be *cis*- and *trans*-*N*,*N*'-diacetyl-*p*-menthane-1,8-diamines by characterisation using X-ray diffraction (Fig. 1 and Table 1).

The IR and ESI$^+$-MS signals of the *cis*- and *trans*- products had values that were very close to each other, consistent with the similar molecular structure of the *cis*- and *trans*- isomers. Each ESI$^+$-MS spectrum of **3a** and **3b** contained a pseudomolecular ion peak of $[M+H]^+$ with an *m/z* value of 255. In the IR spectra, the peak at 3300 cm^{-1} was characteristic of the N–H stretching vibration band in substituted amides. The N–H bending vibration absorption band was found at 1550 cm^{-1}. The peaks at 1640 and 1300 cm^{-1} were characteristic of the C=O and C–N stretching vibration bands.

In the ^{1}H NMR of **3a** (Fig. 2), four singlets at δ values of 1.14, 1.19, 1.75 and 1.78 ppm were assigned to the signals of 9-, 10-, 7-, 1- and 8-methyl groups.

Two singlets at 7.07 and 7.23 ppm were attributed to the 1- and 8-imino protons. Two doublets with chemical shifts of 1.34, 1.37 and 2.20, 2.23 ppm and *J* values of 13.0 Hz corresponded to the axial and equatorial 2-, 6-protons. A triplet (δ 1.88 ppm, *J* 13.0 Hz) was assigned to the 4-proton. Two quartets with δ 1.01, 1.02 ppm, *J* 13.0 Hz) corresponded to the axial 3- and 5-protons, for which the *J* values were identical to the 4-proton. A multiplet with δ values of 1.11–1.16 ppm belonged to the equatorial 3-, 5-protons. As shown in Scheme 1, the *cis*- and *trans*- isomeric diamides differed from each other only in the spatial orientation of the substituents at the C-1 and C-4 positions. Thus, in the ^{1}H NMR spectrum of **3b**, only the signals of the 3-, 5- and 2-, 6-protons differed compared to its isomers **3a**.[15] As shown in



1, **2** **(3~6)a** **(3~6)b**

Scheme 1 Synthesis of *p*-menthane diamides **3a–6b** from turpentine. R = Me- (**3a** and **3b**), Ph- (**4a** and **4b**), Bn- (**5a** and **5b**), *n*-Bu- (**6a** and **6b**).

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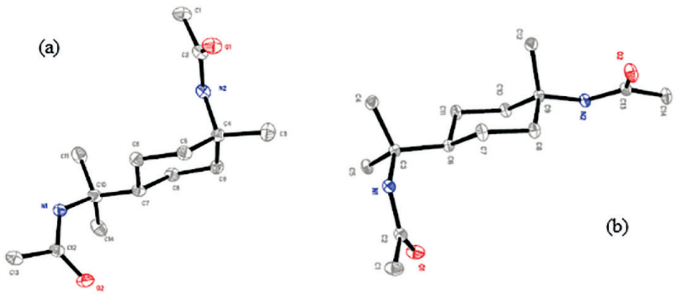


Fig. 1. X-ray crystal structures of *cis*- and *trans*-*N*,*N*'-diacetyl-*p*-menthane-1,8-diamines.

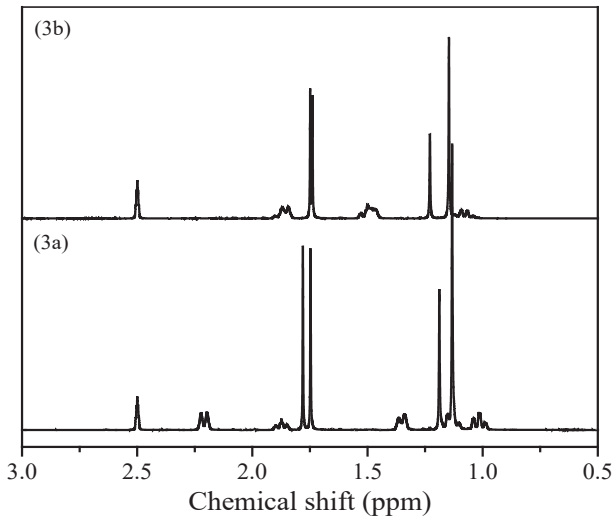


Fig. 2. ^{1}H NMR spectra of *cis*- and *trans*-*N*,*N*'-diacetyl-*p*-menthane-1,8-diamines.

Fig. 2, the triplets of the axial 3- and 5-protons in the ^{1}H NMR spectrum of **3a** changed to quartets in **3b,** and the signals of the equatorial 3-, 5-, axial and equatorial 2-, 6-protons shifted to 1.47–1.53 and 1.85, 1.87 ppm, respectively.

The influences of different conditions on this reaction are summarised in Table 2. From these results, it is clear that the concentration of H_2SO_4 is the critical factor for this reaction. Only trace amount of **3a** and **3b** could be obtained at a mass concentration of H_2SO_4 lower than 20% and the yield increased with increasing H_2SO_4 concentrations and to reach a maximum value of 60.1% at a concentration of H_2SO_4 of 60%. However, the hydrolysis of **3a** and **3b** caused the yield to decrease when the concentration of H_2SO_4 was increased.

Reaction temperature and reaction time are other important factors in this reaction. The results in Table 2 indicated that the yields of **3a** and **3b** increased with increase in the reaction temperature and the extention of the reaction time at the reaction temperature lower than 75 °C and reaction time up to 5 h. Higher reaction temperature and longer reaction time also led to the hydrolysis of the products.

Under optimised conditions, comparative experiments were performed using α-pinene, β-pinene and various nitriles as starting materials to investigate the generality and scope of this reaction. The results are listed in Table 3. It was found that both α- and β-pinene (the main components of turpentine) were rapidly rearranged to the *p*-menthane products. The mole ratio of *cis*- and *trans*- isomers produced from α- and β-pinene were similar to that from turpentine. Different nitriles exhibited different reaction activities and followed a sequence of acetonitrile > *n*-pentanenitrile > phenylacetonitrile > benzonitrile.

Thermodynamic analysis for protic acid-catalysed rearrangements of pinene have been reported in our previous work.[13] The rearrangement mechanism is illustrated in Scheme 2. It appears that the double bond of α- or β-pinene is attacked by H^+ and forms carbocation I as an intermediate.[16] Under the

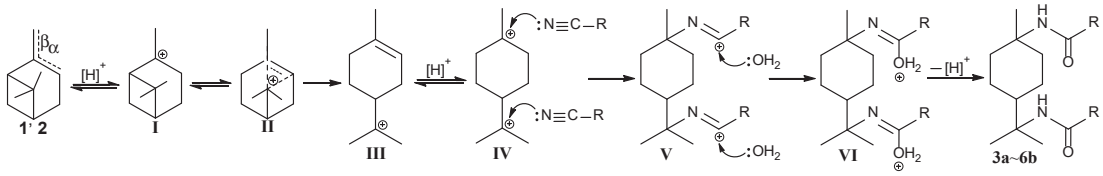
Table 1 Crystallographic data for **3a** and **3b**[a]

	3a	**3b**
Chemical formula	$C_{14}H_{26}N_2O_2$	$C_{14}H_{26}N_2O_2$
Formula weight	254.37	254.37
Temperature (K)	296(2)	296(2)
Crystal system	0.71073 Å	0.71073 Å
Space group	C2/c	P-1
a (Å)	13.9416(9)	6.9321(6)
b (Å)	12.1047(9)	9.7969(9)
c (Å)	18.9084(13)	11.0869(10)
a (deg)	90	76.844(3)
β (deg)	100.123(2)	83.649(3)
g (deg)	90	89.081(3)
V (Å^3)	3141.3(4)	728.65(11)
Z	8	2
ρ_{calc} (mg cm^{-3})	1.076	1.159
Absorp. coeff. (mm^{-1})	0.072	0.077
F(000)	1120	280
θ range (deg.)	2.188 to 25.009	2.135 to 25.005
Reflns collected	11211	5299
Indep. reflns	2764 [R(int) = 0.0562]	2556 [R(int) = 0.0289]
Reflns obs. [$I > 2s(I)$]	1915	2095
Data/restr./paras	2764/0/168	2556/0/168
Goodness of fit	1.064	0.883
R_1/wR_2 [$I > 2s(I)$]	R_1 = 0.0581 wR_2 = 0.1178	R_1 = 0.0457 wR_2 = 0.1207
R_1/wR_2 (all data)	R_1 = 0.0910 wR_2 = 0.1309	R_1 = 0.0586 wR_2 = 0.1310
Largest peak and hole (e×Å^{-3})	0.221 and −0.195	0.205 and −0.198

Table 2 Effects of H_2SO_4 concentration, reaction temperature and reaction time on the yield of **3a** and **3b**[a]

Entry	c/%[b]	Temperature/°C	Time/h	Yield[c]/%
1	20	75	5	0.5
2	40	75	5	28.0
3	50	75	5	36.5
4	60	75	5	60.1
5	70	75	5	34.5
6	80	75	5	13.3
7	60	40	5	16.6
8	60	60	5	31.3
9	60	70	5	51.2
10	60	80	5	43.9
11	60	90	5	12.5
12	60	75	2	26.5
13	60	75	3	36.1
14	60	75	4	52.2
15	60	75	6	53.2
16	60	75	7	40.6

[a]17.0 g turpentine (0.125 mmol), 12.3 g acetonitrile (0.3 mmol), 0.300 mol H_2SO_4 aqueous solution.
[b]Mass concentration of H_2SO_4.
[c]Yields refer to the mixture of **3a** and **3b**.



Scheme 2 Formation mechanism for *p*-menthane diamides **3a–6b** from turpentine.

Table 3 Generality and scope of the reaction[a]

Entry	Pinene-type materials	Nitriles	Yield[b]/%	Ratio of *cis*- to *trans*-products
1	α-Pinene	Acetonitrile	68.3	3.7
2	β-Pinene	Acetonitrile	52.4	3.8
3	Turpentine	Acetonitrile	60.1	3.7
4	Turpentine	Benzonitrile	33.6	3.6
5	Turpentine	Phenylacetonitrile	39.0	3.8
6	Turpentine	*n*-Pentanenitrile	47.8	4.2

[a]0.125 mmol turpentine or pinene, 0.3 mmol nitrile, 0.300 mol 60% H_2SO_4 aqueous solution, 75 °C, 5 h.

[b]Yields refer to the mixture of *cis*- and *trans*- isomers.

effect of H^+, carbocation I became carbonium ion II with a carbon–carbon bond cleavage reaction and then was quickly converted to carbocation III. This was more stable than I and II. Thus, α- or β-pinene were rearranged to carbocation III in relatively high yield. Carbocation III can be obtained *via* the protonation of the double bond by H^+.[17] The resulting carbocation IV is trapped by nitriles and generates a nitrilium ion V, which subsequently reacts with water to produce amide **3a–6b** through the formation of intermediate VI. The substituents in nitriles can sterically hinder the trapping carbocation IV and may hamper the formation of **3a–6b**. Consequently, different nitriles possessed different efficiencies in reaction.

Experimental

Turpentine was of technical grade and distilled (73% α-pinene **1** and 20% β-pinene **2**) before use. Other reagents were of analytical grade and obtained commercially. Melting points were determined on a Kofler hotstage microscope and are uncorrected. ^{1}H NMR spectra were determined on a Bruker Avance III 500 MHz spectrometer. IR spectra were recorded on a Thermo Nicolet IS10 IR instrument. ESI-MS spectra were characterised using a Finnigan TSQ Quantum Mass Spectrometer. GC data were acquired on a Shimadzu GC-2014AF gas chromatography.

Colourless crystals of **3a** and **3b** for single-crystal X-ray diffraction were grown by dissolving the solid in a minimum amount of a mixed solution of ethanol (95%) and ethyl acetate at −18 °C. All data were detected with a Bruker D8 Venture single-crystal diffractometer (Cu Kα, λ = 1.54178 Å), collected with the Bruker APEX2 software and resolved with the Bruker SAINT software. The absorption correction was performed by a semi-empirical method implemented in the SADABS program. The structures were solved by direct methods with the SHELXT program[18] and refined by the least-square methods with the SHELXL-2014 program[19,20] contained in the OLEX2 suite[21]. The non-hydrogen atoms were identified by the SHELXT program directly and refined anisotropically. The hydrogen atoms were located from difference Fourier map inspection and freely refined with Uiso(H) = 1.5Ueq (N, O).

Synthesis and characterisation of p-menthane diamides **3a–6b**; *general procedure*

Turpentine (17.0 g) or pinene (0.125 mmol) and nitriles (0.2 mmol) were added to a four-necked flask. Under continuous mechanical stirring, an aqueous solution of H_2SO_4 (49.0 g, 0.300 mol, 60% wt) was added dropwise over 2 h. The mixture was heated to 75 °C and then nitriles (0.1 mmol) were added and reacted for another 6 h. After the reaction, the resulting mixture was poured into ice water (50 mL), neutralised with 6 mol L^{-1} aqueous solution of NaOH and then extracted with CH_2Cl_2 three times. The organic phase was collected and evaporated to afford crude products and analysed by GC using naphthalene as an internal standard. The crude product was recrystallised or purified by column chromatography to afford pure compounds **3a–6b**.

cis-N,N'-Diacetyl-p-*menthane-1,8-diamine* (**3a**): White solid; yield: 47.3%; m.p. 190–191 °C (lit.[15] 190 °C); IR (cm^{-1}): 3297 (m, ν_{N-H}), 2960 (m, ν_{CH3}), 2923 (m, ν_{CH2}), 1638 (s, $\nu_{C=O}$), 1555 (s, ν_{N-H}), 1442 (m, τ_{CH2}), 1372 (m, τ_{CH3}), 1300 (m, ν_{C-N}), 969 (w), 720 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 1.01, 1.02 (2t, 2H, *J* = 13.0, 3-, 5-H_a), 1.11–1.16 (m, 2H, 3-, 5-H_e), 1.14 (1s, 6H, 9-, 10-CH_3), 1.19 (1s, 3H, 7-CH_3), 1.34, 1.37 (2d, 2H, *J* = 13.0, 2-, 6-H_a), 1.75, 1.78 (2s, 6H, 1-, 8- CH_3), 1.88 (1t, 1H, *J* = 13.0, 4-H), 2.20, 2.23 (1d, 2H, *J* = 13.0, 2-, 6-H_e), 7.07, 7.23 (2s, 2H, 1-, 8-NH); ESI$^+$-MS (15 eV, *m/z*): 255.05 $[M+H]^+$, 196.05 $[M–NH_2COCH_3+H]^+$, 137.05 $[M–2N_2HCOCH_3+H]^+$.

trans-N,N'-Diacetyl-p-*menthane-1,8-diamine* (**3b**): White solid; yield: 12.8%; m.p. 244–245 °C (lit.[15] 244–246 °C); IR (cm^{-1}): 3295 (m, ν_{N-H}), 2964 (m, ν_{CH3}), 2930 (m, ν_{CH2}), 1640 (s, $\nu_{C=O}$), 1547 (s, ν_{N-H}), 1441 (m, τ_{CH2}), 1371 (m, τ_{CH3}), 1299 (m, ν_{C-N}), 970 (w), 720 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 1.07, 1.09 (2q, 2H, *J* = 12.8, 3-, 5-H_a), 1.15 (1s, 6H, 9-, 10-CH_3), 1.23 (1s, 3H, 7-CH_3), 1.47–1.53 (m, 4H, 2-, 6-H_a and 3-, 5-H_e), 1.74, 1.75 (2s, 6H, 1-, 8-CH_3), 1.87 (1t, 1H, *J* = 12.8, 4-H), 1.85, 1.87 (1d, 2H, *J* = 13.0, 2-, 6-H_e), 7.23, 7.34 (2s, 2H, 1-, 8-NH); ESI$^+$-MS (15 eV, *m/z*): 255.15 $[M+H]^+$, 196.08 $[M–NH_2COCH_3+H]^+$, 137.06 $[M–2NH_2COCH_3+H]^+$.

cis-N,N'-Dibenzoyl-p-*menthane-1,8-diamine* (**4a**): White solid; yield: 26.3%; m.p. 152–154 °C (lit.[15] 152–154 °C); IR (cm^{-1}): 3300 (m, ν_{N-H}), 2950 (m, ν_{CH3}), 2856 (w, ν_{CH2}), 1633 (s, $\nu_{C=O}$), 1541 (s, ν_{N-H}), 1450 (m, τ_{CH2}), 1361 (m, τ_{CH3}), 1298 (m, ν_{C-N}), 989 (w), 709 (s); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 1.15, 1.16 (2t, 2H, *J* = 13.0, 3-, 5-H_a), 1.29–1.36 (1m, 2H, 3-, 5-H_e), 1.31, 1.32 (2s, 9H, 7-, 9-, 10-CH_3), 1.48, 1.50 (2d, 2H, *J* = 13.0, 2-, 6-H_e), 2.16 (1t, 1H, *J* = 13.0, 4-H), 2.48, 2.50 (2d, 2H, *J* = 13.0, 2-, 6-H_e), 7.55 (2s, 2H, 1 or 8-NH), 7.40–7.77 (3m, 11H, 1-, 8-C_6H_5, 8 or 1-NH); ESI$^+$-MS (10 eV, *m/z*): 379.14 $[M+H]^+$, 258.12 $[M–NH_2COC_6H_5+H]^+$, 137.13 $[M–2NH_2COCH_3+H]^+$.

trans-N,N'-Dibenzoyl-p-*menthane-1,8-diamine* (**4b**): White solid; yield: 7.3%; m.p. 233–234 °C (lit.[15] 233–235 °C); IR (cm^{-1}): 3318 (m, ν_{N-H}), 2945 (m, ν_{CH3}), 2852 (m, ν_{CH2}), 1634 (s, $\nu_{C=O}$), 1538 (s, ν_{N-H}), 1445 (m, τ_{CH2}), 1377 (m, τ_{CH3}), 1296 (m, ν_{C-N}), 994 (w), 713 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 1.23, 1.25 (2q, 2H, *J* = 12.3, 3-, 5-H_a), 1.33 (1s, 6H, 9-, 10-CH_3), 1.40 (1s, 3H, 7-CH_3), 1.59, 1.61 (2d, 2H, *J* = 12.5, 2-, 6-H_a), 1.70, 1.71 (2d, 2H, *J* = 12.3, 3-, 5-H_e), 2.04, 2.07 (1d, 2H, *J* = 12.5, 2-, 6-H_e), 2.21 (1t, 1H, *J* = 12.3, 4-H), 7.59, 7.64 (2s, 2H, 1-, 8-NH), 7.40–7.44, 7.47–7.51, 7.75–7.78 (3m, 10H, 1-, 8-C_6H_5); ESI$^+$-MS (10 eV, *m/z*): 379.13 $[M+H]^+$, 258.13 $[M–NH_2COC_6H_5+H]^+$, 137.08 $[M–2NH_2COCH_3+H]^+$.

cis-N,N'-Diphenylacetyl-p-*menthane-1,8-diamine* (**5a**): White solid; yield: 30.8%; m.p. 94–95 °C; IR (cm^{-1}): 3291 (m, ν_{N-H}), 2928 (m, ν_{CH3}), 2865 (w, ν_{CH2}), 1639 (s, $\nu_{C=O}$), 1538 (s, ν_{N-H}), 1450 (m, τ_{CH2}), 1358 (m, τ_{CH3}), 1324 (m, ν_{C-N}), 971 (w), 728 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 0.97, 1.00 (2t, 2H, *J* = 12.0, 3-, 5-H_a), 1.05–1.10 (1m, 2H, 3-, 5-H_e), 1.09 (1s, 6H, 9-, 10-CH_3), 1.18 (1s, 3H, 7-CH_3), 1.26, 1.28 (2d, 2H, *J* = 12.0, 2-, 6-H_a), 1.85 (1t, 1H, *J* = 13.0, 4-H), 2.18, 2.16 (2d, 2H, *J* = 13.0, 2-, 6-H_e), 3.34, 3.37 (2s, 4H, 1-, 8-CH_2), 7.17–7.27 (2m, 11H, 1-, 8-C_6H_5, 1- or 8-NH), 7.46 (1s, 1H, 8- or 1-NH); ESI$^+$-MS (15 eV, *m/z*): 407.15 $[M+H]^+$, 272.17 $[M–NH_2COCH_2C_6H_5+H]^+$, 136.14 $[M–2NH_2COCH_3]^+$; HRMS (TOF-MS-

ES⁻) for $C_{26}H_{33}N_2O_2$: Calcd: 405.2542; Found: 405.2538 [M–H]⁻, Δ= −1.0 ppm, DBE = 11.5.

trans-N,N'-Diphenylacetyl-p-*menthane-1,8-diamine* (**5b**): White solid; yield: 8.2%; m.p. 191–193 °C; IR (cm^{-1}): 3309 (m, ν_{N-H}), 2930 (m, ν_{CH3}), 2864 (w, ν_{CH2}), 1643 (s, $\nu_{C=O}$), 1537 (s, ν_{N-H}), 1454 (m, τ_{CH2}), 1352 (m, τ_{CH3}), 1315 (m, ν_{C-N}), 979 (w), 709 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 1.05, 1.08 (q, 2H, *J* = 13.5, 3-, 5-H_a), 1.17 (1s, 6H, 9-, 10-CH_3), 1.22 (1s, 3H, 7-CH_3), 1.42–1.47 (m, 4H, 2-, 6-H_a and 3-, 5-H_e), 1.83–1.87 (1m, 3H, 2-, 6-H_e and 4-H), 3.33, 3.36 (2s, 4H, 1-, 8-CH_2), 7.18–7.29 (2m, 10H, 1-, 8-C_6H_5), 7.44, 7.58 (2s, 2H, 1-, 8-NH); ESI⁺-MS (10 eV, *m/z*): 407.15 $[M+H]^+$, 272.13 $[M–NH_2COCH_2C_6H_5+H]^+$, 136.06 $[M– 2NH_2COCH_3]^+$; HRMS (TOF-MS-ES⁻) for $C_{26}H_{33}N_2O_2$: Calcd: 405.2542; Found: 405.2551 $[M–H]^-$, Δ = 2.2 ppm, DBE = 11.5.

cis-N,N'-Divaleryl-p-*menthane-1,8-diamine* (**6a**): White solid; yield: 38.7%; m.p. 122–125 °C; IR (cm^{-1}): 3265 (m, ν_{N-H}), 2956 (m, ν_{CH3}), 2928 (m, ν_{CH2}), 1639 (s, $\nu_{C=O}$), 1550 (s, ν_{N-H}), 1443 (m, τ_{CH2}), 1365 (m, τ_{CH3}), 1273 (m, ν_{C-N}), 983 (w), 967 (w), 696 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 0.85, 0.86 (2t, 6H, *J* = 7.5, 1-, 8-CH_3), 1.01, 1.02 (2t, 2H, *J* = 13.0, 3-, 5-H_a), 1.11–1.16 (m, 2H, 3-, 5-H_e), 1.13 (1s, 6H, 9-, 10-CH_3), 1.18 (1s, 3H, 7-CH_3), 1.21–1.29 (m, 4H, 1-, 8-$COCH_2CH_2CH_2$), 1.35, 1.37 (2d, 2H, *J* = 13.0, 2-, 6-H_a), 1.42–1.48 (m, 4H, 1-, 8-$COCH_2CH_2$), 1.90 (1t, 2H, *J* = 13.0, 4-H), 2.01, 2.05 (2t, 4H, *J* = 7.5, 1-, 8-$COCH_2$), 2.23, 2.25 (1d, 2H, *J* = 13.0, 2-, 6-H_e), 7.01, 7.16 (2s, 2H, 1-, 8-NH); ESI⁺-MS (15 eV, *m/z*): 339.10 $[M+H]^+$, 238.11 $[M–NH_2CO(CH_2)_3CH_3+H]^+$, 137.01 $[M– 2NH_2CO(CH_2)_3CH_3+H]^+$; HRMS (TOF-MS-ES⁻) for $C_{20}H_{37}N_2O_2$; Calcd: 337.2855; Found: 337.2860 $[M–H]^-$, Δ = 1.5 ppm, DBE = 3.5.

trans-N,N'-Divaleryl-p-*menthane diacetamide* (**6b**): White solid; yield: 9.1%; m.p. 180–181 °C; IR (cm^{-1}): 3319 (m), 3281 (m, ν_{N-H}), 2953 (m, ν_{CH3}), 2931 (m, ν_{CH2}), 1642 (s, $\nu_{C=O}$), 1538 (s, ν_{N-H}), 1450 (m, τ_{CH2}), 1377 (m, τ_{CH3}), 1270 (m, ν_{C-N}), 989 (w), 936 (w), 658 (m); ^{1}H NMR (500 MHz, DMSO-d_6, ppm): δ 0.85 (1t, 6H, *J* = 7.5, 1-, 8-CH_3), 1.07, 1.09 (2q, 2H, *J* = 12.7, 3-, 5-H_a), 1.15 (1s, 6H, 9-, 10-CH_3), 1.23 (1s, 3H, 7-CH_3), 1.20–1.27 (m, 4H, 1-, 8-$COCH_2CH_2$-CH_2), 1.41–1.44 (m, 4H, 1-, 8-$COCH_2CH_2$), 1.46–1.51 (m, 4H, 2-, 6-H_a and 3-, 5-H_e), 1.86–1.92 (1m, 3H, 2-, 6-H_e and 4-H), 1.99, 2.01 (2t, 2H, *J* = 7.5, 1-, 8-$COCH_2$), 7.15, 7.24 (2s, 2H, 1-, 8-NH); ESI⁺-MS (15 eV, *m/z*): 339.19 $[M+H]^+$, 238.18 $[M–NH_2CO(CH_2)_3CH_3+H]^+$, 137.20 $[M–2NH_2CO(CH_2)_3CH_3+H]^+$; HRMS (TOF-MS-ES⁻) for $C_{20}H_{37}N_2O_2$; Calcd: 337.2855; Found: 337.2848 $[M–H]^-$, Δ = −2.1 ppm, DBE = 3.5.

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