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Synthesis and characterization of 3-[(2-{(2-(hydrazinocarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide derivatives

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A series of 3-[(2-{(2-(hydrazinecarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide derivatives containing identically *ortho*-NH/S-substituted benzene moiety were synthesized. The structure of the obtained compounds was proved by combining elemental analysis, mass spectrometry, and ^{1}H, ^{13}C NMR spectroscopy. The $^{1}H/^{13}C$ 2D (HETCOR), $^{1}H/^{1}H$ 2D (COSY), DEPT (^{13}C), NOE (^{1}H) NMR methods and molecular modeling (MM2) were used for structure elucidation in more complicated cases. Supplementary sets of resonances, observed in the ^{1}H and ^{13}C NMR spectra of the majority of synthesized compounds, are explained in terms of peculiar structural features.

Key words: hydrazide, hydrazone, pyrrole, pyrazole, NMR

INTRODUCTION

In recent years, various acid hydrazones have attracted the attention of researchers since they exhibit anticonvulsive [1], anti-inflammatory, antithrombotic [2], antimicrobial [3–5], and antiproliferative activities [6]. Hydrazides of *N*-substituted β-alanines find application as intermediate compounds in the synthesis of various heterocyclic systems such as oxadiazoles [7–9], thiadiazoles [9–12], triazoles [9, 12], pyrazoles [13–16], and pyrroles [17].

A literature survey has revealed problems in the synthesis of various hydrazide derivatives and complications of their structural investigations [18–46]. The majority of compounds containing an amide and / or azomethine group exist as mixtures of isomers in solutions [18–37]. The formation of inseparable isomers depends on the solvent used [18, 21, 37]. NMR spectra of such compounds are the result of statistically averaged molecular characteristics depending on a dynamic process such as conformational equilibrium as well as intra and / or intermolecular interactions. Some studies were devoted to the synthesis of hydrazide derivatives containing a CONHN=C fragment in single [18, 19, 42], double [20–22, 43, 44], and fourfold side chains [23]. Continuing our interest in the synthesis of *N*-substituted β-amino acids and their derivatives [20–23, 42–46], we report herein the synthesis and characterization of hydrazide derivatives possessing *ortho*-NH/S-substituted benzene.

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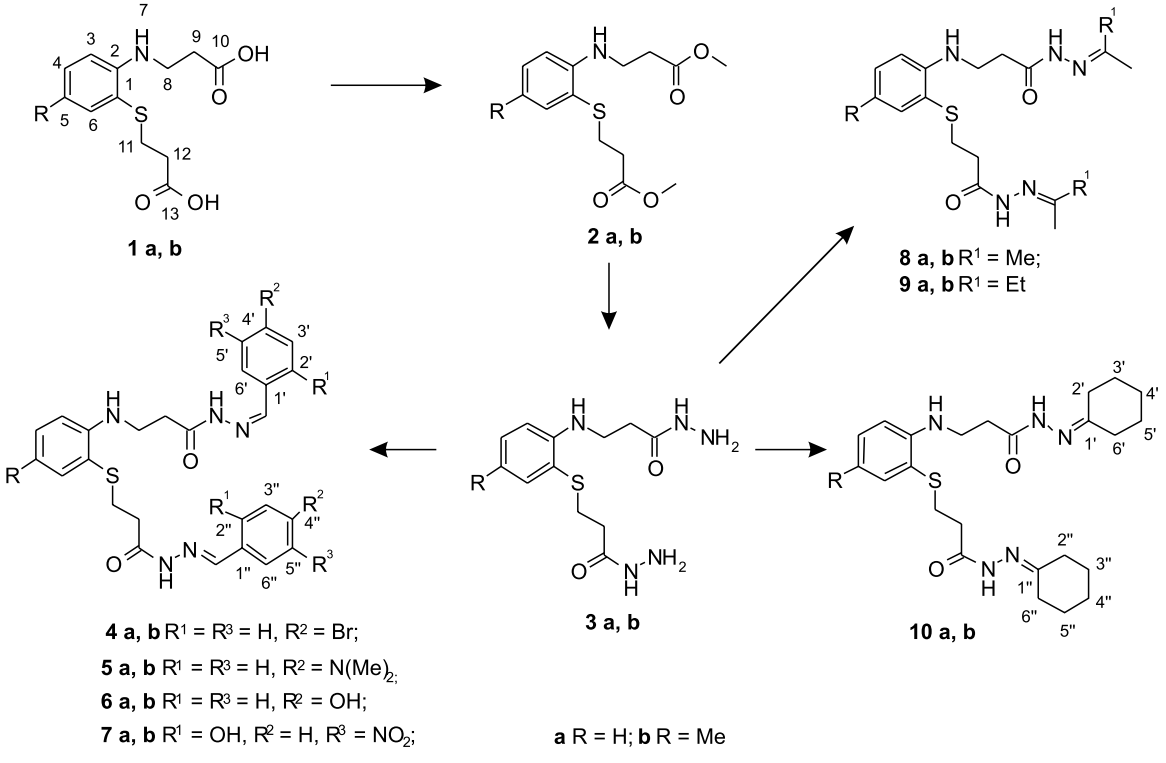
RESULTS AND DISCUSSION

Hydrazides of dicarboxylic acids **1** were obtained from aminophenols and acrylic acid as reported previously [45, 46]. Esterification of **1** with methanol in the presence of a catalytic amount of sulfuric acid afforded the corresponding esters **2** as resin-like products (Scheme 1).

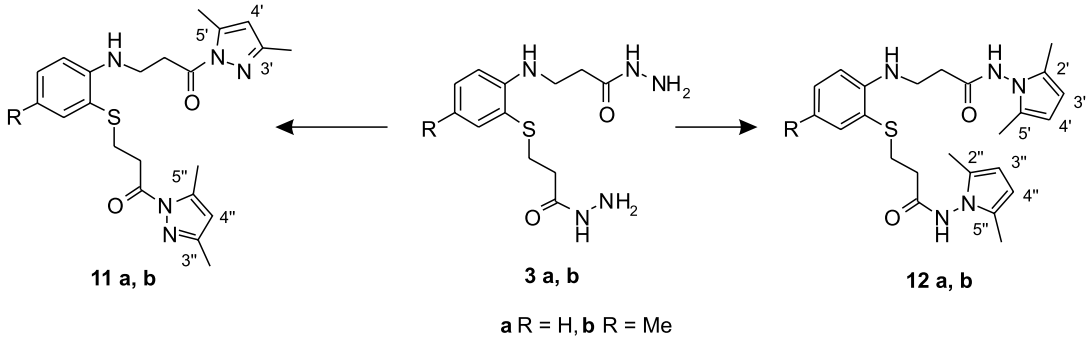
Dihydrazides **3** were synthesized by the reaction of **2** dissolved in ethanol with hydrazine at room temperature. Hydrazones of 3-[2-(2-carboxyethylamino)phenyl-(5-methylphenyl)sulfanyl]propanoic acid **4–10** were synthesized in up to 97% yield by heating under reflux the reaction mixtures of dihydrazides **3** and acetone, 2-butanone, cyclohexanone, or aromatic aldehydes.

Reaction of **3** with 2,3-pentanedione in 2-propanol in the presence of a catalytic amount of hydrochloric acid provided **11** containing a 3,5-dimethylpyrazole moiety (Scheme 2). Whereas, reaction of **3** with 2,5-hexanedione in the presence of a catalytic amount of acetic acid afforded dihydrazones **12** containing a 3,5-dimethylpyrrole fragment.

The structure of the synthesized compounds **1–12** was determined by NMR spectroscopy. The assignment of the spectral lines was carried out using the chemical shift theory [47], signal intensity and multiplicity arguments, spin–spin coupling constant values, and by comparison with structurally related compounds [48]. The ^{1}H and ^{13}C NMR spectral data are presented in the Experimental section. Carbon atoms are marked arbitrarily according to the numbering given in Schemes 1 and 2.



Scheme 1. Synthesis of hydrazone derivatives



Scheme 2. Synthesis of pyrazole and pyrrole derivatives

The $^{1}H/^{13}C$ 2D (HETCOR) and $^{1}H/^{1}H$ 2D (COSY) NMR techniques were used to confirm the assignment of resonances in ^{1}H and ^{13}C NMR spectra of the core benzene moiety. This part of the molecule required special attention since compounds **4–7** possess another benzene ring in the azomethine group.

The multiplet paterns observed in the ^{1}H NMR spectra of **1–12** are characteristic of 1,2-disubstituted (**a**) and 1,2,5-trisubstituted (**b**) benzenes. The resonances in ^{13}C NMR spectra of the core benzene moiety differ not much among compounds of **a** and **b** type. It has been noted that C-2 and C-5 atoms are sensitive to 5-substituent; consequently, C-2 is shielded by ~2 ppm, and C-5 is deshielded by ~9 ppm for compounds of **b** type in respect to the ones of **a** type. The assignment of resonances of C-1 and C-5 (δ, ~116 ppm) was performed using DEPT spectra.

While analysing the NMR spectra of the NH/S side chain moiety of **a** and **b** type compounds **4–10**, attention was focused on the presence of amide and azomethine fragments in them. The solubility of compounds containing amide fragment in nonpolar solvents is limited; therefore, the majority of NMR spectra have been recorded using DMSO-d_6 as a solvent. Such compounds participate in intermolecular hydrogen bonding (S=O ··· HN) determining a hindered rotation around the CO-NH bond and formation of rotamers. The splitting of resonances of atoms neighbouring an amide group (up to 4 bonds) was observed in such case. Due to the presence of the lone pair of a nitrogen atom in the azomethine fragments, an additional splitting of substituent atom resonances was observed in the ^{1}H and ^{13}C NMR spectra. Consequently, two isomerism centers originating from the azomethine and amide group determine sixteen different isomers which can be formed in solution of **4–10**. As a result of the dynamic process, only a few isomeric structures exist long enough to be presented in NMR spectra. Actually, the NMR spectra reflect the time-averaged structures of the study compounds in solutions. No correlation was found between the total steric energy values obtained for models of **4–10** isomers and the NMR data; therefore, it is evident that none of the isomers is predominant. The NMR spectra recorded in $CDCl_3$ are more intricate than the ones in DMSO-d_6 solution [21].

The isomer composition of compounds related to hydrazide derivatives mentioned above was examined elsewhere [18–22, 44]. It has been shown that in case of a CONHN=C fragment in a single side chain four isomers [18], and in the case of double side chain ten isomers [44] are present in the DMSO-d_6 solution.

The NMR spectra specifically reflect the influence of substituents in an azomethine group on the structural features of **4–10** [44]. The most complicated spectra are observed for compounds 7 due to an *ortho*-OH group involved into the formation of hydrogen bonds. The NMR spectra of compounds **8** and **9** were analysed using previously published [18, 21] data on the analogous compounds.

Molecules of compounds **10** possess the azomethine group included in the cyclohexanone moiety. ^{13}C NMR spectra revealed that the cyclohexanone ring carbons were affected by the lone pair of the nitrogen atom in the azomethine group. The distribution of the resonances of the cyclohexanone ring carbons showed a trend similar to that of resonances of the substituents of the azomethine group in **8** and **9**. The difference in the chemical shifts of cyclohexanone ring carbons C-2' and C-6' was about 8 ppm, and the difference in those of C-3' and C-5' was about 2 ppm.

Protons and carbons of 3,5-dimethylpyrazole moiety in **11** were found to resonate in the expected region. The NOE (^{1}H) and $^{1}H/^{13}C$ 2D (HETCOR) NMR techniques assisted in the assignment of resonances in this case. The difference in the chemical shift values of pyrazole methyl resonances in NH/S side chains was about 0.03 ppm in the ^{1}H and ^{13}C NMR spectra.

Compounds **12** possess the amide fragment determining formation of the above-mentioned rotamers in DMSO-d_6 solutions. Traces (7%) of other isomers of **12** were observed only in the ^{1}H NMR spectra. The rotation around the CO-NH bond was investigated using the molecular modeling techniques. Theoretically, **12** can exist as a mixture of four isomeric structures ($Z_{NH}Z_S$, $E_{NH}Z_S$, $Z_{NH}E_S$, $E_{NH}E_S$). The calculated values of total steric energies for optimized models of **12b** isomers were 6.07, 15.73, 25.82, and 3.64 kJ/mol, respectively.

The values of rotation barriers (Table) of optimized models showed the rotation around the amide bond to be dependent both on the isomer structure and on the NH/S type of the side chain. It has been clearly shown that the most mobile amide bonds exist in the $E_{NH}E_S$ isomer. This isomer has the minimal total steric energy and is observed as a dominant (93%) one in the ^{1}H NMR spectrum. This allowed us to conclude that the rotation around the CO-NH bond encounters high restrictions caused by the voluminous 2,5-dimethylpyrrole ring.

All S-side chain atoms are more shielded as compared to NH ones; consequently, two sets of resonances shifted in respect to each other are observed in the NMR spectra [48].

The differences in chemical shift values of methylene groups in compounds of **a** and **b** type are negligible. Due to the presence of an amide fragment and an azomethine group, the splitting of resonances of atoms in methylene groups by 0.1–0.8 ppm in ^{13}C NMR and by ~0.1 ppm in ^{1}H NMR with various intensity ratio is observed in both of the side chains.

Table. **Rotation barriers around amide bond of the model of 12b isomers**

Side chain type	Rotation barriers (kJ/mol) of isomeric structures			
	$Z_{NH}Z_S$	$E_{NH}Z_S$	$Z_{NH}E_S$	$E_{NH}E_S$
-NH-	2724.33	5309.71	60.84	62.22
-S-	105.94	146.02	137.57	82.01

EXPERIMENTAL

Melting points were determined with an automatic APA1 melting point apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a *Varian Unity Inova* (300 MHz, 75 MHz) spectrometer operating in the Fourier transform mode. Chemical shifts (δ) are reported in parts per million (ppm) calibrated from TMS (0 ppm) as an internal standard for ^{1}H NMR, and DMSO-d_6 (39.50 ppm) or $CDCl_3$ (77.00 ppm) for ^{13}C NMR. Mass spectra were obtained on a Waters (Micromas) ZQ 2000 spectrometer. Elemental analyses (C, H, N) were performed with an Elemental Analyzer CE-440. The monitoring of the reaction course and the purity of the synthesized compounds was carried out using TLC on Silufol 254, Silufol UV-254, and Alugram SIL G/UV_{254} plates.

The molecular modeling of the study compounds was carried out using Chem 3D Ultra 9.0 (Licence Cambridge Software Package, Serial number: 031 406391 4800).

N-[2-(2-Carboxyethylsulfanyl)phenyl]-β-alanine **(1a)** was synthesized as described previously [45]. M. p. 129–130 °C (2-propanol).

N-{2-[(2-Carboxyethyl)sulfanyl]-4-methylphenyl}-β-alanine **(1b)** was synthesized as described previously [46]. M. p. 155–156.5 °C (2-propanol–water).

N-[2-(2-Methoxycarbonylethyl)sulfanyl]-β-alanine methyl ester **(2a)**. A mixture of diacid **1a** (6.725 g, 25 mmol), methanol (30 ml, 0.75 mol) and concentrated H_2SO_4 (1.2 ml) was heated under reflux for 8 h, cooled to room temperature, diluted with water (20 ml) and neutralised with Na_2CO_3. The product was extracted from the aqueous solution with diethyl ether (20 × 3 ml). Diethyl ether was removed with a rotary evaporator. Yield 4.5 g (61%), resin-like substance. ^{1}H NMR (DMSO-d_6) δ: 2.49 (t, 2H, J = 7.0 Hz, 12-CH_2); 2.63 (t, 2H, J = 6.6 Hz, 9-CH_2); 2.86 (t, 2H, J = 7.1 Hz, 11-CH_2); 3.41 (t, 2H, J = 6.6 Hz, 8-CH_2); 3.58 (s, 3H, 13-COO$\underline{CH_3}$); 3.61 (s, 3H, 10-COO$\underline{CH_3}$); 5.48 (br. s, 1H, 7-NH); 6.57 (dt, 1H, J = 1.1 Hz, J = 7.5 Hz, 5-H_{ar}); 6.66 (dd, 1H, J = 1.2 Hz, J = 7.5 Hz, 3-H_{ar}); 7.19 (dt, 1H, J = 1.6 Hz, J = 7.1 Hz, 4-H_{ar}); 7.30 (dd, 1H, J = 1.6 Hz, J = 7.6 Hz, 6-H_{ar}). ^{13}C NMR (DMSO-d_6) δ: 28.89 (C-11); 33.13 (C-12); 33.63 (C-9); 38.64 (C-8); 51.39 ((C-13-)-OCH_3); 51.45 ((C-10)-OCH_3); 110.02 (C-3); 115.80 (C-1); 116.32 (C-5); 130.28 (C-4); 136.00 (C-6); 148.51 (C-2); 171.72 (C-13); 172.20 (C-10). MS (CI, 20 V), *m/z* (%): 298.4 $[M]^+$ (88). Anal. calcd. for $C_{14}H_{19}NO_4S$, %: C, 56.5; H, 6.44; N, 4.71. Found, %: C, 56.82; H, 6.45; N, 4.72.

N-{[2-(2-Methoxycarbonylethyl)sulfanyl]-5-methylphenyl}-β-alanine methyl ester **(2b)** was prepared from diacid **1b** (2.5 g, 8.8 mmol), methanol (30 ml) and concentrated H_2SO_4 (1.0 ml) according to **2a** synthesis procedure. Yield 1.67 g. (61%), resin-like substance. ^{1}H NMR (DMSO-d6) δ: 2.15 (s, 3H, 5-CH_3); 2.48 (t, 2H, J = 7.0 Hz, 12-CH_2); 2.60 (t, 2H, J = 6.5 Hz, 9-CH_2); 2.85 (t, 2H, J = 7.0 Hz, 11-CH_2); 3.37 (q, 2H, J = 6.5 Hz, 8-CH_2); 3.57 (s, 3H, 13-COO$\underline{CH_3}$); 3.60 (s, 3H, 10-COO$\underline{CH_3}$); 5.31 (t, 1H, J = 6.2 Hz, 7-NH); 6.57 (d, 1H, J = 8.3 Hz, 3-H_{ar}); 7.00 (dd, 1H, J = 2.1 Hz, J = 8.3 Hz, 4-H_{ar}); 7.13 (d, 1H, J = 2.1 Hz, 6-H_{ar}). ^{13}C NMR (DMSO-d_6) δ: 19.73 (5-CH_3); 28.96 (C-11); 33.17 (C-12); 33.68 (C-9); 38.89 (C-8); 51.38 (13-COO$\underline{CH_3}$); 51.44 (10-COO$\underline{CH_3}$); 110.22 (C-3); 115.85 (C-1); 124.96 (C-5); 130.75 (C-4); 136.17 (C-6); 146.34 (C-2); 171.74 (13-$\underline{C}OOCH_3$); 172.24 (10-$\underline{C}OOCH_3$). MS (CI, 20 V), *m/z* (%): 312.4 $[M]^+$ (88). Anal. calcd. for $C_{15}H_{21}NO_4S$, %: C, 57.86; H, 6.80; N, 4.50. Found, %: C, 58.01; H, 6.83; N, 4.52.

3-[(2-{(2-(Hydrazinocarbonyl)ethyl)sulfanyl}phenyl)amino]propanehydrazide **(3a)**. To a stirred solution of diester **2a** (4.25 g, 0.14 mol) in ethanol (30 ml), hydrazine hydrate (5 ml) was added dropwise, and the reaction mixture was stirred for 8 h. The crystals formed were filtered off and recrystallised from 2-propanol. Yield 3.6 g (85%). M. p. 104–105 °C. ^{1}H NMR (DMSO-d_6) δ: 2.23 (t, 2H, J = 7.3 Hz, 12-CH_2); 2.36 (t, 2H, J = 6.5 Hz, 9-CH_2); 2.84 (t, 2H, J = 7.3 Hz, 11-CH_2); 3.34 (q, 2H, J = 6.5 Hz, 8-CH_2); 4.36 (br. s, 2H, NH_2); 5.54 (t, 1H, J = 6.0 Hz, 7-NH); 6.56 (dt, 1H, J = 1.1 Hz, J = 7.4 Hz, 5-H_{ar}); 6.63 (dd, 1H, J = 1.0 Hz, J = 8.2 Hz, 3-H_{ar}); 7.17 (dt, 1H, J = 1.6 Hz, J = 8.2 Hz, 4-H_{ar}); 7.30 (dd, 1H, J = 1.6 Hz, J = 7.5 Hz, 6-H_{ar}); 9.04 (s, 1H, 13-CONH); 9.11 (s, 1H, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 29.70 (C-11); 32.88 (C-12); 33.41 (C-9); 39.78 (C-8); 109.87 (C-3); 116.09 (C-5); 116.29 (C-1); 129.96 (C-4); 135.50 (C-6); 148.50 (C-2); 169.80 (C-13); 170.25 (C-10). MS (CI, 20 V), *m/z* (%): 298.4 $[M]^+$ (100). Anal. calcd. for $C_{12}H_{19}N_5O_2S$, %: C, 48.47; H, 6.44; N, 23.55. Found, %: C, 48.45; H, 6.48; N, 23.88.

3-[(2-{(2-(Hydrazinocarbonyl)ethyl)sulfanyl}-4-methylphenyl)amino]propanehydrazide **(3b)**. A mixture of ester **2b** (1.6 g, 5.1 mmol) dissolved in ethanol (30 ml) and hydrazine hydrate (5 ml) was stirred at room temperature for 24 h. The liquid fraction was removed with a rotary evaporator; diethyl ether (20 ml) was poured on the oil-like residue and was kept at 6 °C for 24 h. The precipitate was filtered off and washed with diethyl ether. Yield 1.38 g (86%). M. p. 95–96 °C. ^{1}H NMR (DMSO-d_6) δ: 2.15 (s, 3H, 5-CH_3); 2.23 (t, 2H, J = 7.3 Hz, 12-CH_2); 2.34 (t, 2H, J = 6.5 Hz, 9-CH_2); 2.86 (t, 2H, J = 7.3 Hz, 11-CH_2); 3.30 (q, 2H, J = 6.5 Hz, 8-CH_2); 4.26 (br. s, 4H, NH_2); 5.33 (t, 1H, J = 5.9 Hz, 7-NH); 6.55 (d, 1H, J = 8.3 Hz, 3-H_{ar}); 6.98 (dd, 1H, J = 1.7 Hz, J = 8.2 Hz, 4-H_{ar}); 7.13 (d, 1H, J = 1.7 Hz, 6-H_{ar}); 9.07 (s, 1H, 13-CONH); 9.11 (s, 1H, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 19.82 (5-CH_3); 29.78 (C-11); 32.96 (C-12); 33.48 (C-9); 39.78 (C-8); 110.10 (C-3); 116.36 (C-1); 124.72(C-5); 130.47 (C-4); 135.79 (C-6); 146.44 (C-2); 169.88 (C-13); 170.36 (C-10). MS (CI, 20 V), *m/z* (%): 321.4 $[M]^+$ (100), 238.4 $[M\text{-}74]^+$ (52). Anal. calcd. for $C_{13}H_{21}N_5O_2S$, %: C, 50.14; H, 6.80; N, 22.49. Found, %: C, 49.92; H, 6.91; N, 22.58.

N^1-[(4-Bromophenyl)methylene]-3-({2-[(2-{N^1-[(4-bromophenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]phenyl}amino)propanehydrazide **(4a)**. To a solution of hydrazide **3a** (0.375 g, 1.25 mmol) in methanol (10 ml), a

solution of 4-bromobenzaldehyde (1.0 g, 5 mmol) in methanol (10 ml) was added. The reaction mixture was heated under reflux for 2 h and cooled to room temperature. The precipitate was filtered off, washed with warm methanol and diethyl ether. Yield 0.74 g (93%). M. p. 175–176 °C. ^{1}H NMR (DMSO-d_6) δ: 2.37–2.57 (m, 2H, 12-CH_2); 2.75–2.97 (m, 4H, 9, 11-CH_2); 3.32–3.49 (m, 2H, 8-CH_2); 5.59–5.72 (m, 1H, 7-NH); 6.54–6.62 (m, 1H, 5-H_{ar}); 6.71–6.75 (m, 1H, 3-H_{ar}); 7.18–7.25 (m, 1H, 4-H_{ar}); 7.30–7.35 (m, 1H, 6-H_{ar}); 7.42–7.61 (m, 4H, (2", 2', 3", 3', 5", 5', 6", 6')-H_{ar}); 7.88–8.10 (7 s, 2H, N=CH" + N=CH'); 11.40–11.53 (5s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 29.15, 29.32, 29.57 (C-11); 31.60, 31.67, 32.19 (C-12); 33.73, 33.82, 34.20, 34.82 (C-9); 38.82 (C-8); 109.89, 110.02 (C-3); 116.12 (C-5); 116.29 (C-1); 122.87, 123.15 (C-4" + C-4'); 128.44, 128.54 (C-3", C-5"); 128.85 (C-3', C-5'); 130.10, 130.19 (C-4); 131.70, 131.74 (C-2", C-6" + C-2', C-6'); 133.43, 133.54 (C-1" + C-1'); 135.71, 135.95, 136.07 (C-6); 141.58, 144.88 (N=C"); 141.65, 144.88 (N=C'); 148.69, 148.84 (C-2); 166.89, 172.62 (13-CONH); 167.46, 167.54, 173.24 (10-CONH). MS (CI, 20 V), *m/z* (%): 634.0 $[M+2]^+$ (15), 632.0 $[M]^+$ (30). Anal. calcd. for $C_{26}H_{25}N_5O_2S$, %: C, 49.46; H, 3.99; N, 11.09. Found, %: C, 49.18; H, 3.97; N, 11.03.

N¹-[(4-Bromophenyl)methylene]-3-({2-[(2-{N¹-[(4-bromophenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]-4-methylphenyl}amino)propanehydrazide **(4b)** was prepared from **3b** (0.62 g, 2.0 mmol) and 4-bromobenzaldehyde (1.6 g, 8.0 mmol) according to **4a** synthesis procedure. Yield 1.09 g (85%). M. p. 173–174 °C. ^{1}H NMR (DMSO-d_6) δ: 2.09, 2.16 (2 s, 3H, 5-CH_3); 2.37–2.56 (m, 2H, 12-CH_2); 2.75–2.95 (m, 4H, 9, 11-CH_2); 3.39–3.49 (m, 2H, 8-CH_2); 5.48 (br. s, 1H, 7-NH); 6.62–6.66 (m, 1H, 3-H_{ar}); 7.00–7.17 (m. 2H, 4, 6-H_{ar}); 7.42–7.67 (m, 4H, (2', 2", 3", 3', 5", 5', 6", 6')-H_{ar}); 7.88–8.10 (7s, 2H, N=CH" + N=CH'); 11.41–11.52 (5s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 19.78, 19.84 (5-CH_3); 29.05, 29.36, 29.62 (C-11); 31.61, 31.68, 32.13 (C-12); 33.76, 33.88, 34.30, 34.43 (C-9); 39.08 (C-8); 110.11, 110.24 (C-3); 116.11, 116.18, 116.29 (C-1); 122.85, 123.14 (C-4", C-4'); 124.67, 124.79 (C-5); 128.41, 128.45, 128.53, 128.84 (C-3", C-5", C-3', C-5'); 130.57, 130.67 (C-4); 131.68, 131.74 (C-2", C-5", C-2', C-5'); 133.44, 133.54, 133.56 (C-1", C-1'); 135.87, 136.24, 136.38 (C-6); 141.53, 141.59, 144.86 (N=C"); 141.77, 141.82, 144.93 (N=C'); 146.43, 146.49, 146.57, 146.66 (C-2); 166.90, 172.62 (13-CONH); 167.50, 167.58, 173.29 (10-CONH). MS (CI, 20 V), *m/z* (%): 667.9 $[M+Na]^+$ (100), 646.0 $[M]^+$ (20), 502.1 $[M-144]^+$ (70). Anal. calcd. for $C_{27}H_{27}N_5O_2S$, %: C, 50.25; H, 4.22; N, 10.85. Found, %: C, 50.62; H, 4.27; N, 11.03.

N¹-{[4-(Dimethylamino)phenyl]methylene}-3-[(2-{[2-(N¹-{[4-(dimethylamino)phenyl]methylene}hydrazinecarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide **(5a)**. To a solution of hydrazide **3a** (0.298 g, 1 mmol) in methanol (10 ml), a solution of 4-(dimethylamino)benzaldehyde (1.2 g, 8 mmol) in methanol (10 ml) was added and the reaction mixture was heated under reflux for 3 h. The crystals formed were filtered off, washed with water and diethyl ether. Yield 0.33 g (48%). M. p. 171–172 °C. ^{1}H NMR (DMSO-d_6) δ: 2.33–2.51 (m, 2H, 12-CH_2); 2.70–3.09 (m, 4H, 9, 11-CH_2 + 12H, 4", 4'-$N(CH_3)_2$); 3.36–3.49 (m, 2H, 8-CH_2); 5.60–5.80 (m, 1H, 7-NH); 6.55–6.77 (m, 2H, 5, 3-H_{ar} + 4H, (3", 5", 3', 5')-H_{ar}); 7.18–7.47 (m, 2H, 4, 6-H_{ar} + 4H, (2", 6", 2', 6')-H_{ar}); 7.81, 7.87, 8.00 (3s, 2H, N=CH" + N=CH'); 11.07–11.19 (4 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 29.19, 29.56, 29.86 (C-11); 31.83, 32.29 (C-12); 33.71, 33.86, 34.30 (C-9); 39.77 ($N(CH_3)_2$); 39.77 (C-8); 109.91 (C-3); 111.75 (C-3", C-5", C-3', C-5'); 116.12, 116.23 (C-5); 116.41 (C-1); 121.59 (C-1", C-1'); 127.93, 127.99, 128.32 (C-2", C-5", C-2', C-5'); 130.09 (C-4); 135.62, 135.69, 135.87, 135.97 (C-6); 143.63, 143.71, 146.98 (N=C"); 143.98, 147.14 (N=C'); 148.70, 148.88 (C-2); 151.23, 151.38 (C-4", C-4'); 166.15, 166.21, 171.99 (13-CONH); 166.69, 166.87, 172.50 (10-CONH). MS (CI, 20 V), *m/z* (%): 560.73 $[M]^+$ (30). Anal. calcd. for $C_{30}H_{37}N_7O_2S$, %: C, 64.37; H, 6.66; N, 17.52. Found, %: C, 64.42; H, 6.60; N, 17.37.

N¹-{[4-(Dimethylamino)phenyl]methylene}-3-[(2-{[2-(N¹-{[4-(dimethylamino)phenyl]methylene}hydrazinecarbonyl)ethyl]sulfanyl}-4-methylphenyl)amino]propanehydrazide **(5b)** was prepared from **3b** (0.311 g, 1 mmol) and 4-(dimethylamino)benzaldehyde (1.2 g, 8 mmol) according to **5a** synthesis procedure. Yield 0.45 g (785%). M. p. 185–186°C. ^{1}H NMR (DMSO-d_6) δ: 2.12, 2.16 (2 s, 3H, 5-CH_3); 2.33–2.51 (m, 2H, 12-CH_2); 2.74–2.98 (m, 4H, 9, 11-CH_2 + 12H, 4", 4'-$N(CH_3)_2$); 3.35–3.45 (m, 2H, 8-CH_2); 5.44, 5.52 (2 br. s, 1H, 7-NH); 6.59–6.72 (m, 1H, 3-H_{ar} + 4H, (3", 5", 3', 5')-H_{ar}); 7.01–7.04 (m, 1H, 4-H_{ar}); 7.14, 7.16 (2s, 1H, 6-H_{ar}); 6.33–7.49 (m, 4H, (2", 6", 2', 6')-H_{ar}); 7.81–7.99 (5s, 2H, N=CH" + N=CH'); 11.06–11.18 (5s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 19.84 (5-CH_3); 29.18, 29.60, 29.94 (C-11); 31.83, 32.31 (C-12); 33.75, 33.93, 34.38 (C-9); 39.78 ($N(CH_3)_2$); 39.78 (C-8); 110.09, 110.18 (C-3); 111.76 (C-3", C-5" + C-3', C-5'); 116.27, 116.40 (C-1); 121.55, 121.63 (C-1", C-1'); 124.62, 124.74, 124.87 (C-5); 127.90, 128.02, 128.34 (C-2", C-6", C-2', C-6'); 130.63 (C-4); 135.81, 135.21, 136.32 (C-6); 143.60, 143.69, 146.53, 146.63 (N=C"); 143.94, 146.75 (N=C'); 146.97, 147.14 (C-1); 151.23, 151.40 (C-4", C-4'); 166.19, 166.25, 172.00 (13-CONH); 166.77, 166.96, 172.60 (10-CONH). MS (CI, 20 V), *m/z* (%): 596.3 $[M+Na]^+$ (100), 574.3 $[M]^+$, (25). Anal. calcd. for $C_{30}H_{37}N_7O_2S$, %: C, 64.89; H, 6.85; N, 17.24. Found, %: C, 64.56; H, 6.92; N, 17.24.

N¹-[(4-Hydroxyphenyl)methylene]-3-({2-[(2-{N¹-[(4-hydroxyphenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]phenyl}amino)propanehydrazide **(6a)**. To a solution of hydrazide **3a** (0.744 g, 2.5 mmol) in methanol (20 ml), a solution of 4-hydroxybenzaldehyde (1.8 g, 15 mmol) in methanol (10 ml) was added, and the reaction mixture was heated under reflux for 8 h. The precipitate was filtered off, washed with water, and recrystallised from 2-propanol. Yield 0.84 g (67%). M. p. 140–141°C. ^{1}H NMR (DMSO-d_6) δ: 2.34–2.55 (m, 2H, 12-CH_2); 2.73–2.94 (m, 4H, 9, 11-CH_2); 3.42–3.47 (m,

2H, 8-CH_2); 5.69 (br. s, 1H, 7-NH); 6.53–6.62 (m, 1H, 5-H_{ar}); 6.69–6.81 (m, 1H, 3-H_{ar} + 4H, (3", 5", 3', 5')-H_{ar}); 7.16–7.51 (m, 6H, (2", 6", 2', 6')-H_{ar} + 4, 6-H_{ar}); 7.83–8.03 (4s, 2H, N=CH" + N=CH'); 9.87 (br. s, 2H, 13, 10-CONH); 11.15–11.28 ((4 s, 2H, (4", 4')-OH). ^{13}C NMR (DMSO-d_6) δ: 29.13 (C-11); 31.74, 32.24 (C-12); 33.80, 34.25 (C-9); 39.78 (C-8); 109.90, 109.96 (C-3); 115.63, 115.84 (C-3", C-5", C-3', C-5'); 116.04, 116.13, 116.17, 116.23, 116.33 (C-1, C-5); 125.20 (C-1", C-1'); 128.36, 128.44, 128.75 (C-2", C-6", C-2', C-5'); 130.07 (C-4); 135.63, 135.89, 135.95 (C-6); 143.13, 143.16, 146.47, 146.52, 146.56 (N=C"); 143.45, 146.66, 146.70 (N=C'); 148.71, 148.80 (C-2); 159.07, 159.28 (C-4", C-4'); 166.38, 166.45, 172.20, (13-CONH); 166.93, 167.12, 172.76 (10-CONH). MS (CI, 20 V), *m/z* (%): 528.3 $[M+Na]^+$ (100), 506.4 $[M]^+$ (20). Anal. calcd. for $C_{26}H_{27}N_5O_4S$, %: C, 61.77; H, 5.38; N, 12.85. Found, %: C, 61.48; H, 5.35; N, 12.78.

N¹-[(4-Hydroxyphenyl)methylene]-3-({2-[(2-{N¹-[(4-hydroxyphenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]-4-methylphenyl}amino)propanehydrazide **(6b)** was prepared from **3b** (0.31 g, 1 mmol) and 4-hydroxybenzaldehyde (0.72 g, 6 mmol) according to **6a** synthesis procedure. Recrystallised from ethanol. Yield 0.39 g (75%). M. p. 181–182 °C. ^{1}H NMR (DMSO-d_6) δ: 2.11, 2.66 (2 s, 3H, 5-CH_3); 2.34–2.51 (m, 2H, 12-CH_2); 2.75–2.94 (m, 4H, 9, 11-CH_2); 3.37–3.43 (m, 2H, 8-CH_2); 5.25 (br. s, 1H, 7-NH); 6.61–6.67 (m, 1H, 3-H_{ar}); 6.74–6.81 (m, 4H, (3", 5", 3', 5')-H_{ar}); 6.98–7.04 (m, 1H, 4-H_{ar}); 7.14, 7.16 (2 s, 1H, 6-H_{ar}); 6.35–7.51 (m, 4H, (2", 6", 2', 6')-H_{ar}); 7.84–8.03 (4 s, 2H, N=CH" + N=CH'); 9.87, 9.88, 9.90 (3 s, 2H, 13, 10-CONH); 11.15–11.27 (5 s, 2H, (4", 4')-OH). ^{13}C NMR (DMSO-d_6) δ: 19.79, 19.85 (5-CH_3); 29.05, 29.44 (C-11); 31.76, 32.22 (C-12); 33.80, 33.88, 34.34 (C-9); 40.33 (C-8); 110.08, 110.15 (C-3); 115.63 (C-3", C-5", C-3', C-5'); 116.23, 116.31, 116.40 (C-1); 124.59, 124.71 (C-5); 125.23 (C-1", C-1'); 128.31, 128.44, 128.75 (C-2", C-6", C-2', C-6'); 130.48, 130.61 (C-4); 135.82, 136.25, 136.34 (C-6); 143.10, 146.45 (N=CH"); 143.39, 143.41, 146.69 (N=CH'); 146.59, 146.69 (C-1", C-1'); 159.07, 159.29 (C-4", C-4'); 166.41, 166.49, 172.21 (13-CONH); 167.00, 167.26, 172.81 (10-CONH). MS (CI, 20 V), *m/z* (%): 542.7 $[M+Na]^+$ (100), 520.7 $[M]^+$ (60). Anal. calcd. for $C_{27}H_{29}N_5O_4S$, %: C, 62.41; H, 5.56; N, 13.48. Found, %: C, 62.56; H, 5.66; N, 13.52.

N¹-[(2-Hydroxy-5-nitrophenyl)methylene]-3-({2-[(2-{N¹-[(2-hydroxy-5-nitrophenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]phenyl}amino)propanehydrazide **(7a)**. A mixture of dihydrazide **3a** (0.375 g, 1.25 mmol), 2-hydroxy-5-nitrobenzaldehyde (1.25 g, 7.5 mmol), and methanol (30 ml) was heated under reflux for 5 h. The precipitate was filtered off, washed with ethanol and diethyl ether. Yield 0.65 g (87%). M. p. 153–154 °C. ^{1}H NMR (DMSO-d_6) δ: 2.38–2.60 (m, 2H, 12-CH_2); 2.84 (t, (0.5)2H, J = 6.9 Hz, 9-CH_2); 2.90–3.07 (m, ((0.5)2H, 9-CH_2 + 2H, 11-CH_2); 3.33–3.50 (m, 2H, 8-CH_2); 5.63, 5.71 (br. s, 1H, 7-NH); 6.44–8.49 (m, 12H, H_{ar} + N=CH" + N=CH'); 11.48–12.51 (13, 10-CONH + 2H, (2", 2')-OH). ^{13}C NMR (DMSO-d_6) δ: 28.89, 29.24, 29.76 (C-11); 31.63, 31.68, 31.83 (C-12); 33.50, 33.68, 34.02, 34.29 (C-9); 39.78 (C-8); 110.07 (C-3); 116.09, 116.16, 116.21 (C-1); 116.32, 116.38 (C-5); 116.58, 116.99 (C-3", C-3'); 119.74, 121.13 (C-1", C-1'); 121.23, 121.33, 123.82, 123.92 (C-6", C-6'); 126.26, 126.33, 126.42 (C-4", C-4'); 130.20 (C-4); 135.81, 135.95 (C-6); 137.55, 137.77, 137.83 (C-5", C-5'); 139.79, 142.80 (13-N=C"); 139.93, 142.99 (10-N=C'); 148.69, 148.72, 148.84 (C-2); 161.79, 162.52 (C-2", C-2'); 166.91, 167.00, 172.55 (13-CONH); 167.59, 167.63, 173.21 (10-CONH). MS (CI, 20 V), *m/z* (%): 596.2 $[M]^+$ (30). Anal. calcd. for $C_{26}H_{25}N_7O_8S$, %: C, 52.43; H, 4.23; N, 16.46. Found, %: C, 52.54; H, 4.30; N, 16.60.

N¹-[(2-Hydroxy-5-nitrophenyl)methylene]-3-({2-[(2-{N¹-[(2-hydroxy-5-nitrophenyl)methylene]hydrazinocarbonyl}ethyl)sulfanyl]-4-methylphenyl}amino)propanehydrazide **(7b)** was prepared from dihydrazide **3b** (0.311 g, 1 mmol), 2-hydroxy-5-nitrobenzaldehyde (1.0 g, 6 mmol), and ethanol (30 ml) according to **7a** synthesis procedure. Yield 0.5 g (82%). M. p. 144–145 °C. ^{1}H NMR (DMSO-d_6) δ: 2.03, 2.07, 2.14, 2.17 (4 s, 3H, 5-CH_3); 2.39–2.58 (m, 2H, 12-CH_2); 2.82–3.00 (m, 4H, 9, 11-CH_2); 3.29–3.50 (m, 2H, 8-CH_2); 5.38–5.50 (br. m, 1H, 7-NH); 6.60–8.49 (m, 11H, H_{ar} + (N=CH" + N=CH')); 11.47–11.83 (6 s, (2", 2')-OH + 10, 13-CONH). ^{13}C NMR (DMSO-d_6) δ: 19.62, 19.79 (5-CH_3); 28.78, 29.25, 29.75 (C-11); 31.66, 31.70 (C-12); 33.51, 33.72, 34.09, 34.35 (C-9); 39.78 (C-8); 110.07 (C-3); 116.08, 116.18, 116.28 (C-1); 116.56, 116.97 (C-3", C-3'); 119.70, 121.11 (C-1", C-1'); 121.24, 121.32, 123.83, 123.92 (C-6", C-6'); 124.64, 124.79, 124.97 (C-5); 126.08, 126.19, 126.26, 126.37, 126.63 (C-4", C-4'); 130.65, 130.83, 130.20 (C-4); 135.89, 136.01, 136.14, 136.32 (C-6); 137.54, 137.72, 137.78 (C-5", C-5'); 139.72, 139.79, 142.84 (N=C"); 139.91 143.02 (N=C'); 146.48, 146.61 (C-2); 161.75, 162.49 (C-2", C-1'); 166.88, 166.97, 172.48 (13-CONH); 167.63, 173.21 (10-CONH). MS (CI, 20 V), *m/z* (%): 632.1 $[M+Na]^+$ (65); 610.1 $[M]^+$ (35). Anal. calcd. for $C_{27}H_{27}N_7O_8S$, %: C, 53.2; H, 4.46; N, 16.08. Found, %: C, 53.46; H, 4.72; N, 16.06.

N¹-(Propan-2-ylidene)-3-[(2-{[2-(N¹-propan-2-ylidenehydrazinocarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide **(8a)**. A mixture of **3a** (1.49 g, 5 mmol) and acetone (15 ml, 0.2 mol) was heated under reflux for 4 h. The precipitate was filtered off, washed with diethyl ether and recrystallised from methanol. Yield 1.45 g (83%). M. p. 126–127 °C. ^{1}H NMR (DMSO-d_6) δ: 1.81–1.91 (9 s, 12H, 13, 10-N=C(CH_3)$_2$); 2.40 (dt, (0.5)2H, J = 2.3 Hz, J = 7.2 Hz, 12-CH_2); 2.51–2.57 (m, (0.5)2H, 12-CH_2); 2.69 (t, (0.5)2H, J = 7.1 Hz, 9-CH_2); 2.80 (t, (0.5)2H, J = 6.8 Hz, 9-CH_2); 2.87 (t, 2H, J = 7.1 Hz, 11-CH_2); 3.40 (dd, 2H, J = 6.4 Hz, J = 12.6 Hz, 8-CH_2); 5.45–5.64 (m, 1H, 7-NH); 6.53–7.31 (m, 4H, H_{ar}); 9.99–10.10 (5 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 16.95, 17.01 (*cis*-CH_3"); 17.47, 17.53 (*cis*-CH_3'); 24.90 (*trans*-CH_3"); 25.09, 25.14 (*trans*-CH_3'); 28.86, 29.52 (C-11); 32.04, 32.38 (C-12); 33.36, 33.50, 33.59, 33.93, 33.98 (C-9); 39.80 (C-8); 109.92 (C-3);

116.04, 116.17 (C-5); 116.53 (C-1); 129.80, 129.97 (C-4); 135.33 (C-6); 148.57 (C-2); 150.12, 154.96 (N=C''); 150.43 155.19 (N=C'); 166.57, 166.70, 172.51 (13-CONH); 167.12, 167.28, 173.09 (10-CONH). MS (CI, 20 V), *m/z* (%): 378.56 $[M]^+$ (50). Anal. calcd. for $C_{18}H_{27}N_5O_2S$, %: C, 57.27; H, 7.21; N, 18.55. Found, %: C, 57.59; H, 7.22; N, 18.57.

***N¹-(Propan-2-ylidene)-3-[(2-{[2-(N¹-propan-2-ylidenehydrazinocarbonyl)ethyl]sulfanyl}-4-methylphenyl)amino] propanehydrazide* (8b)**. A mixture of dihydrazide **3b** (0.31 g, 1 mmol) and acetone (20 ml) was heated under reflux for 3 h. The precipitate was filtered off and washed with diethyl ether. Yield 0.31 g (79%). M. p. 82–83 °C. ^{1}H NMR (DMSO-d_6) δ: 1.81–1.90 (8 s, 12H, N=C(CH_3)$_2$'' + N=C(CH_3)$_2$'); 2.14, 2.15 (2 s, 3H, 5-CH_3); 2.40 (dt, (0.6)2H, *J* = 2.3 Hz, *J* = 7.2 Hz, 12-CH_2); 2.49–2.56 (m, (0.4)2H, 12-CH_2); 2.69 (t, (0.5)2H, *J* = 7.2 Hz, 9-CH_2); 2.77 (t, (0.5)2H, *J* = 6.8 Hz, 9-CH_2); 2.86 (t, 2H, *J* = 7.2 Hz, 11-CH_2); 3.34–3.85 (m, 2H, 8-CH_2); 5.28–5.44 (m, 1H, 7-NH); 6.63, 6.58 (2d, 1H, *J* = 8.3 Hz, 3-H_{ar}); 6.99 (d, 1H, *J* = 8.5 Hz, 4-H_{ar}); 7.12 (s, 1H, 6-H_{ar}); 10.01–10.12 (6 s, 2H, 13,10-CONH). ^{1}H NMR ($CDCl_3$) δ: 1.75–2.07 (12 s, 12H, N=C(CH_3)$_2$'' + N=C(CH_3)$_2$'); 2.20, 2.21 (2 s, 3H, 5-CH_3); 2.41–3.54 (m, 8H, (11, 12, 9, 8)-CH_2); 5.22 (br. s, 1H, 7-NH); 6.55–7.31 (m, 3H, (3, 4, 6)-H_{ar}); 8.04–9.39 (12 br. s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 16.99, 17.05 (*cis*-CH_3''); 17.56 (*cis*-CH_3'); 19.80 (5-CH_3); 24.95 (*trans*-CH_3''); 25.18 (*trans*-CH_3'); 28.98, 29.50, 29.94 (C-11); 32.10, 32.33 (C-12); 33.41, 33.56, 33.94, 34.02 (C-9); 39.78, 40.05 (C-8); 110.22 (C-3); 116.36, 116.51, 116.61 (C-1); 124.56, 124.64, 124.80 (C-5); 130.37, 130.49 (C-4); 135.76 (C-6); 146.51 (C-2); 150.22, 154.93 (C=N''); 150.43, 155.14 (C=N'); 166.67, 166.75, 172.59 (13-CONH); 167.22, 167.40, 173.19 (10-CONH). ^{13}C NMR ($CDCl_3$) δ: 16.02, 16.89 (*cis*-CH_3''); 16.13, 17.16 (*cis*-CH_3'); 20.09 (5-CH_3); 25.40 (*trans*-CH_3'' + *trans*-CH_3'); 29.55, 29.90 (C-11); 32.30, 32.45, 32.79 (C-12); 35.12, 35.20, 35.35 (C-9); 39.35, 39.62, 40.89 (C-8); 110.16, 110.23 (C-3); 116.93, 118.09 (C-1); 125.58, 127.09 (C-5); 130.61, 130.79, 131.03 (C-4); 136.58, 136.76, 137.03 (C-6); 146.52 (C-2); 146.74, 149.22 (C=N''); 146.86, 149.68 (C=N'); 167.57, 173.61 (13-CONH); 168.15, 168.80, 173.93 (10-CONH). MS (CI, 20 V), *m/z* (%): 414.60 $[M+Na]^+$ (100). Anal. calcd. for $C_{19}H_{29}N_5O_2S$, %: C, 58.28; H, 7.47; N, 17.89. Found, %: C, 58.41; H, 7.62; N, 17.62.

***N¹-(Butan-2-ylidene)-3-[(2-{[2-(N¹-butan-2-ylidenehydrazinocarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide* (9a)**. A mixture of **3a** (1.49 g, 5 mmol) and 2-butanone (1.6 ml, 20 mmol) was heated under reflux for 4 h. The reaction mixture was cooled to room temperature, the precipitate was filtered off, washed with diethyl ether, and recrystallised from acetone. Yield 1.01 g (50%). M. p. 57–58 °C (acetone–water). ^{1}H NMR (DMSO-d_6) δ: 0.92–1.05 (m, 6H, N=CCH_2C$\underline{H}_3$'' + N=CCH_2C$\underline{H}_3$'); 1.79–1.90 (7 s, 6H, N=C(CH_3)'' + N=C(CH_3)'); 2.12, 2.31 (m, 4H, N=C$\underline{H}_2$CH_3'' + N=CC$\underline{H}_2$CH_3'); 2.38–2.59 (m, (0.5)2H, 12-CH_2); 2.53–2.59 (m, (0.5)2H, 12-CH_2); 2.68–2.90 (m, 4H, 9-CH_2 + 11-CH_2); 3.29–3.44 (m, 2H, 8-CH_2); 5.48–5.65 (m, 1H, 7-NH); 6.52–6.60 (m, 1H, 5-H_{ar}); 6.68 (dt, 1H, *J* = 1.4 Hz, *J* = 8.0 Hz, 3-H_{ar}); 7.14–7.18 (m, 1H, 4-H_{ar}); 7.28–7.33 (m, 1H, 6-H_{ar}); 9.97–10,20 (9 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 9.71, 9.75, 9.80 (*cis*-$CH_2\underline{C}H_3$'' + *cis*-$CH_2\underline{C}H_3$'); 10.30, 10.54, 10.79 (*trans*-$CH_2\underline{C}H_3$'' + *trans*-$CH_2\underline{C}H_3$'); 15.69,15.76 (*cis*-CH_3'' + *cis*-CH_3'); 15.90, 15.96 (*trans*-CH_3'' + *trans*-CH_3'); 22.10, 22.45, 22.90, 23.35 (*cis*-$\underline{C}H_2CH_3$'' + *cis*-$\underline{C}H_2CH_3$'); 28.90, 28.95, 29.57 (C-11); 31.26, 31.48 (*trans*-$\underline{C}H_2CH_3$'' + *trans*-$\underline{C}H_2CH_3$'); 32.05, 32.48, 32.55 (C-12); 33.57, 34.01 (C-9); 39.05 (C-8); 109.84, 109.93, 110.01 (C-3); 115.96, 116.01, 116.08, 116.20 (C-5); 116.38, 116.44, 116.50, 116.53 (C-1); 129.85, 129.94, 129.98 (C-4); 135.36, 135.44, 135.57 (C-6); 148.59, 148.69 (C-2); 153.52, 153.59, 158.52 (N=C''); 153.90, 153.97 158.70, 158.79. 158.90 (N=C'); 166.68, 166.74, 172.76 (13-CONH); 167.43, 167.56, 173.33 (10-CONH). MS (CI, 20 V), *m/z* (%): 406.5 $[M]^+$ (50). Anal. calcd. for $C_{20}H_{31}N_5O_2S$, %: C, 58.23; H, 7.7; N, 17.27. Found, %: C, 58.28; H, 7.67; N, 17.38.

***N¹-(Butan-2-ylidene)-3-[(2-{[2-(N¹-butan-2-ylidenehydrazinocarbonyl)ethyl]sulfanyl}-4-methylphenyl)amino]propanehydrazide* (9b)**. A mixture of **3b** (0.311 g, 1 mmol) and 2-butanone (3.2 ml, 40 mmol) was heated under reflux for 5 h. The precipitate was filtered off, washed with 2-propanol and diethyl ether. Yield 0.32 g (72%). M. p. 95–96 °C. ^{1}H NMR (DMSO-d_6) δ: 0.91–1.03 (m, 6H, N=CCH_2C$\underline{H}_3$'' + N=CCH_2C$\underline{H}_3$'); 1.79–1.90 (7 s, 6H, N=C(CH_3)'' + N=C(CH_3)'); 2.08, 2.09 (2s, 3H, 5-CH_3); 2.14–2.24 (m, 4H, N=CC$\underline{H}_2CH_3$'' + N=CC$\underline{H}_2CH_3$'); 2.37–2.57 (m, 2H, 12-CH_2); 2.67–2.89 (m, 4H, 9-CH_2 + 11-CH_2); 3.29–3.42 (m, 2H, 8-CH_2); 5.29–5.43 (m, 1H, 7-NH); 6.56–6.62 (m, 1H, 3-H_{ar}); 6.97–7.01 (m, 1H, 4-H_{ar}); 7.11–7.14 (m, 1H, 6-H_{ar}); 9.98–10.21 (10s, 2H, 13, 10-CONH). ^{1}H NMR ($CDCl_3$) δ: 1.01–1.15 (m, 6H, N=CCH_2C$\underline{H}_3$'' + N=CCH_2C$\underline{H}_3$'); 1.73–1.99 (11 s, 6H, N=C(CH_3)'' + N=C(CH_3)'); 2.18–2.50 (m, 7H, 5-CH_3 + N=CC$\underline{H}_2CH_3$'' + N=CC$\underline{H}_2CH_3$'); 2.67–3.05 (m, 6H, 12-CH_2 + 9-CH_2 + 11-CH_2); 3.50–3.56 (m, 2H, 8-CH_2); 5.21 (br. s, 1H, 7-NH); 6.58–6.65 (m, 1H, 3-H_{ar}); 6.99–7.04 (m, 1H, 4-H_{ar}); 7.22–7.28 (m, 1H, 6-H_{ar}); 8.53–9.97 (12 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 9.79 (*cis*-$CH_2\underline{C}H_3$'' + *cis*-$CH_2\underline{C}H_3$'); 10.31, 10.61, 10.87 (*trans*-$CH_2\underline{C}H_3$'' + *trans*-$CH_2\underline{C}H_3$'); 15.76, 15.87 (*cis*-CH_3'' + *cis*-CH_3'); 16.00 (*trans*-CH_3'' + *trans*-CH_3'); 19.80 (5-CH_3); 22.10, 22.45, 22.90, 23.35 (*cis*-$\underline{C}H_2CH_3$'' + *cis*-$\underline{C}H_2CH_3$'); 28.96, 29.41, 29.51, 29.99 (C-11); 31.41, 31.55 (*trans*-$\underline{C}H_2CH_3$'' + *trans*-$\underline{C}H_2CH_3$'); 32.11, 32.57 (C-12); 33.46, 33.64, 34.03 (C-9); 39.78 (C-8); 110.08, 110.17, 110.26 (C-3); 116.33, 116.51 (C-1); 124.55, 124.66, 124.83 (C-5); 130.44 (C-4); 135.68, 135.82, 136.01 (C-6); 146.61 (C-2); 153.46, 153.53, 158.43 (N=C''); 153.88, 153.95 158.62, 158.70 (N=C'); 166.75, 166.81, 172.84 (13-CONH); 167.33, 167.54, 173.43 (10-CONH). ^{13}C NMR ($CDCl_3$) δ: 9.64 (*cis*-$CH_2\underline{C}H_3$'' + *cis*-$CH_2\underline{C}H_3$'); 10.26, 10.50, 11.08 (*trans*-$CH_2\underline{C}H_3$'' + *trans*-$CH_2\underline{C}H_3$'); 14.89 (*cis*-CH_3'' + *cis*-CH_3'); 16.05, 16.51, 16.91 (*trans*-CH_3'' + *trans*-CH_3'); 20.08 (5-CH_3); 22.74, 23.63, 25.40 (*cis*-$\underline{C}H_2CH_3$'' + *cis*-$\underline{C}H_2CH_3$'); 29.47, 29.56, 30.53,

30.90 (C-11); 32.00, 32.09 (*trans*-$\underline{C}H_2CH_3$'' + *trans*-$\underline{C}H_2CH_3$'); 32.24, 32.48 (C-12); 33.02 (C-9); 39.39, 39.65, 40.88, 40.95 (C-8); 110.17, 110.26 (C-3); 116.84 (C-1); 125.06, 125.57 (C-5); 130.66 (C-4); 136.76, 136.89, 137.05 (C-6); 146.80 (C-2); 152.81, 153.41, 155.61 (N=C'' + N=C'); 173.79 (13-CONH); 174.10 (10-CONH). MS (CI, 20 V), *m/z* (%): 442.4 $[M+Na]^+$ (100), 404.4 $[M-15]^+$ (20), 388.4 $[M-30]^+$ (60). Anal. calcd. for $C_{21}H_{33}N_5O_2S$, %: C, 60.11; H, 7.93; N, 16.69. Found, %: C, 60.55; H, 7.95; N, 16.50.

***N-Cyclohexylidene-3-[(2-{[2-(N¹-cyclohexylidenehydrazinocarbonyl)ethyl]sulfanyl}phenyl)amino]propanehydrazide* (10a)**. A mixture of hydrazide **3a** (0.75 g, 2.5 mmol) dissolved in methanol (10 ml) and cyclohexanone (5 ml, 0.05 mol) was heated under reflux for 4 h. Liquid fractions were removed on a rotary evaporator, the precipitate was washed with water and diethyl ether. Yield 0.64 g (56%). M. p. 59–60°C. ^{1}H NMR (DMSO-d_6) δ: 1.48–1.68 (m, 12H, (3'', 3', 4'', 4', 5'', 5')-CH_2); 2.12–2.41 (m, 8H, (2'', 2', 6'', 6')-CH_2 + (0.5)2H, 12-CH_2); 2.49–2.56 (m, (0.5)2H, 12-CH_2); 2.70 (t, (0.5)2H, *J* = 7.2 Hz, 9-CH_2); 2.81 (t, (0.5)2H, *J* = 7.2 Hz, 9-CH_2); 2.86–2.90 (m, 2H, 11-CH_2); 3.36–3.44 (m, 2H, 8-CH_2); 5.47–5.67 (m, 1H, 7-NH); 6.53–6.60 (m, 1H, 5-H_{ar}); 6.65–6.72 (m, 1H, 3-H_{ar}); 7.14–7.20 (m, 1H, 4-H_{ar}); 7.30 (d, 1H, *J* = 7.2 Hz, 6-H_{ar}); 10.16–10.29 (5 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 25.10 (C-3'', C-3'); 25.62 (C-4'', C-4'); 26.44 (C-2''); 27.19 (C-2'); 26.86 (C-5'', C-5'); 28.92, 29.56 (C-11); 32.01, 32.32 (C-12); 33.40, 33.56, 33.98 (C-9); 34.92 (C-6''); 35.09 (C-6'); 39.78 (C-8); 109.91 (C-3); 116.02 (C-5); 116.35, 116.51 (C-1); 129.81 (C-4); 135.34, 135.57 (C-6); 148.60, 148.69, 149.00 (C-2); 155.55, 160.59 (C-1'' + C-1'); 155.76, 160.88, 161.02 (C-1'' + 1'); 166.80, 172.53, (13-CONH); 167.28, 167.47, 173.30 (10-CONH). MS (CI, 20 V), *m/z* (%): 457.6 $[M+Na]^+$ (100), 458.5 $[M]^+$ (20). Anal. calcd. for $C_{24}H_{35}N_5O_2S$, %: C, 63.00; H, 7.71; N, 15.18. Found, %: C, 62.91; H, 7.82; N, 14.98.

***N-Cyclohexylidene-3-([2-{[2-(N¹-cyclohexylidenehydrazinocarbonyl)ethyl]sulfanyl}-4-methylphenyl)amino]propanehydrazide* (10b)** was prepared from dihydrazide **3b** (2.33 g, 7.5 mmol) in methanol (10 ml) and cyclohexanone (10 ml, 0.01 mmol) according to **10a** synthesis procedure. Liquid fractions were decanted, water was poured on the resin-like residue, the precipitate was filtered off and washed with water. Yield 2.0 g (57%). M. p. 72–73 °C. ^{1}H NMR (DMSO-d_6) δ: 1.55–1.91 (m, 12H, (3'', 3', 4'', 4', 5'', 5')-CH_2); 2.15–2.47 (m, 8H, (2'', 2', 6'', 6')-CH_2 + (0.5)2H, 12-CH_2 + 3H, 5-CH_3); 2.64–2.68 (m, (0.5)2H, 12-CH_2); 2.85–3.04 (m, 4H, 9-CH_2 + 11-CH_2); 3.47–3.56 (m, 2H, 8-CH_2); 5.25 (br. s, 1H, 7-NH); 6.54–6.64 (m, 1H, 3-H_{ar}); 6.99–7.04 (m, 1H, 4-H_{ar}); 7.21–7.26 (m, 1H, 6-H_{ar}); 8.77–9.62 (7 s, 2H, 13, 10-CONH). ^{1}H NMR ($CDCl_3$) δ: 1.54–1.71 (m, 12H, (3'', 3', 4'', 4', 5'', 5')-CH_2); 2.15–2.46 (m, 8H, (2'', 2', 6'', 6')-CH_2 + (0.5)2H, 12-CH_2 + 3H, 5-CH_3); 2.63–2.67 (m, (0.5)2H, 12-CH_2); 2.83–3.03 (m, 4H, 9-CH_2 + 11-CH_2); 3.46–3.55 (m, 2H, 8-CH_2); 5.23 (br. s, 1H, 7-NH); 6.54–6.64 (m, 1H, 3-H_{ar}); 6.97–7.03 (m, 1H, 4-H_{ar}); 7.20–7.24 (m, 1H, 6-H_{ar}); 8.76–9.61 (7 br. s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 19.80 (5-CH_3); 25.15 (C-3'', C-3'); 25.60, 25.70 (C-2'' + C-2'); 26.47 (C-4''); 26.91 (C-5'', C-5'); 27.23 (C-4'); 29.01, 29.07, 29.55 (C-11); 32.09, 32.31, 32.36 (C-12); 33.45, 33.65, 34.11 (C-9); 34.96, 35.15 (C-6'' + C-6'); 39.78 (C-8); 110.22 (C-3); 116.37, 116.51, 116.57, 116.64 (C-1); 124.55, 124.66, 124.80 (C-5); 130.36, 130.52 (C-4); 135.71, 135.85 (C-6); 146.49, 146.58 (C-2); 155.51, 155.56, 160.58 (C-1''); 155.74, 155.79, 160.80, 160.90, 161.03, 161.22 (C-1'); 166.85, 166.90, 172.70 (13-CONH); 167.40, 167.62, 173.40 (10-CONH). ^{13}C NMR ($CDCl_3$) δ: 20.10 (5-CH_3); 25.51, 25.54 (C-3'', C-3'); 25.78 (C-2'', C-2'); 25.96, 26.05 (C-4'' + C-4'); 26.95, 26.97 (C-5'', C-5'); 29.58, 29.75 (C-11); 31.13, 31.79, 32.19 (C-12); 32.40, 32.74 (C-9); 35.49 (C-6'' + C-6'); 39.29, 39.64, 40.86, 41.95 (C-8); 110.14, 110.59, 111.07 (C-3); 116.96, 117.12 (C-1); 125.52, 125.95, 126.59, 126.80 (C-5); 130.54, 130.79, 130.96, 131.11 (C-4); 136.57, 136.67, 137.04, 137.26 (C-6); 146.51, 146.71, 146.84, 146.97 (C-2); 155.54, 155.76, 161.49, 161.77 (C-1''); 156.09, 156.35. 162.12, 162.87 (C-1'); 167.78, 168.09, 173.74, 173.77 (13-CONH); 168.39, 168.44, 174.08, 174.24 (10-CONH). MS (CI, 20 V), *m/z* (%): 494.7 $[M+Na]^+$ (100). Anal. calcd. for $C_{25}H_{37}N_5O_2S$, %: C, 63.66; H, 7.91, N; 14.85. Found, %: C, 63.64; H, 7.97; N, 14.92.

***1-(3,5-Dimethyl-1H-pyrazol-1-yl)-3-[(2-{[3-(3,5-dimethyl-1H-pyrazol-1-yl)-3-oxopropyl]sulfanyl}phenyl)amino]propan-1-one* (11a)**. A mixture of **3a** (0.75 g, 2.5 mmol), 2,4-pentanedione (1.1 ml, 10 mmol), 2-propanol (8 ml), and few drops of HCl was heated under reflux for 3h. The crystals formed were filtered off, washed with methanol and diethyl ether. Yield 0.54 g (48%). M. p. 64–65 °C. ^{1}H NMR (DMSO-d_6) δ: 2.12 (s, 3H, 3''-CH_3); 2.17 (s, 3H, 3'-CH_3); 2.42 (s, 3H, 5''-CH_3); 2.44 (s, 3H, 5'-CH_3); 2.96 (t, 2H, *J* = 6.9 Hz, 12-CH_2); 3.22 (t, 2H, *J* = 6.9 Hz, 9-CH_2); 3.32 (t, 2H, *J* = 6.6 Hz, 11-CH_2); 3.52 (q, 2H, *J* = 6.3 Hz, 8-CH_2); 5.63 (t, 1H, *J* = 6.3 Hz, 7-NH); 6.13 (s, 1H, 4''-CH); 6.15 (s, 1H, 4'-CH); 6.56 (dt, 1H, *J* = 0.6 Hz, *J* = 7.3 Hz, 5-H_{ar}); 6.62 (dd, 1H, *J* = 0.5 Hz, *J* = 7.9 Hz, 3-H_{ar}); 7.19 (dt, 1H, *J* = 1.5 Hz, *J* = 7.9 Hz, 4-H_{ar}); 7.30 (dd, 1H, *J* = 1.5 Hz, *J* = 7.6 Hz, 6-H_{ar}). ^{13}C NMR (DMSO-d_6) δ: 13.41 (3''-CH_3); 13.44 (3'-CH_3); 14.01 (5''-CH_3); 14.04 (5'-CH_3); 28.37 (C-11); 34.47 (C-12); 34.84 (C-9); 38.56 (C-8); 110.00 (C-3); 111.18 (C-4'', C-4'); 116.10 (C-1); 116.23 (C-5); 130.11 (C-4); 135.62 (C-6); 143.20 (C-3'', C-3'); 148.53 (C-2); 151.45 (C-5'', C-5'); 171.58 (C-13); 172.19 (C-10). MS (CI, 20 V), *m/z* (%): 426.6 $[M]^+$ (100). Anal. calcd. for $C_{22}H_{27}N_5O_2S$, %: C, 62.10; H, 6.40; N, 16.50. Found, %: C, 62.36; H, 6.53; N, 16.53.

***1-(3,5-Dimethyl-1H-pyrazol-1-yl)-3-[(2-{[3-(3,5-dimethyl-1H-pyrazol-1-yl)-3-oxopropyl]sulfanyl}-4-methylphenyl)amino]propan-1-one* (11b)**. A mixture of dihydrazide **3b** (0.311 g, 1 mmol), 2,4-pentanedione (1.1 g, 10 mmol), 2-propanol (8 ml) and HCl (2 ml) was heated under reflux for 5 h. The reaction mixture was cooled to room temperature, the precipitate was filtered off and

washed with water. Yield 0.4 g (91%). M. p. 111–112 °C. ^{1}H NMR (DMSO-d_6) δ: 2.13 (s, 6H, 3"-CH_3 + 5-CH_3); 2.17 (s, 3H, 3'-CH_3); 2.41 (d, 3H, *J* = 0.7 Hz, 5"-CH_3); 2.44 (d, 3H, *J* = 0.7 Hz, 5'-CH_3); 2.95 (t, 2H, *J* = 6.9 Hz, 12-CH_2); 3.22 (t, 2H, *J* = 6.8 Hz, 9-CH_2); 3.30 (t, 2H, *J* = 6.8 Hz, 11-CH_2); 3.47 (q, 2H, *J* = 6.3 Hz, 8-CH_2); 5.42 (t, 1H, *J* = 6.3 Hz, 7-NH); 6.14 (q, 1H, *J* = 0.7 Hz, 4"-CH); 6.15 (q, 1H, *J* = 0.7 Hz, 4'-CH); 6.64 (d, 1H, *J* = 8.3 Hz, 3-H_{ar}); 7.00 (dd, 1H, *J* = 1.7 Hz, *J* = 8.2 Hz, 4-H_{ar}), 7.11 (dd, 1H, *J* = 1.5 Hz, *J* = 8.2 Hz, 6-H_{ar}). ^{13}C NMR (DMSO-d_6) δ: 13.41 ((C-3")-CH_3); 13.44 ((C-3')-CH_3); 14.01 ((C-5")-CH_3); 14.44 ((C-5')-CH_3); 19.70 (5-CH_3); 28.44 (C-11); 34.50 (C-12); 34.80 (C-9); 38.80 (C-8); 110.19 (C-3); 111.18 (C-4", C-4'); 116.04 (C-1); 124.82 (C-5); 130.61 (C-4); 135.91 (C-6); 143.20 (C-3", C-3'); 146.38 (C-2); 151.44 (C-5", C-5'); 171.59 (C-13); 172.24 (C-10). MS (CI, 20 V), *m/z* (%): 462.3[M+Na]$^+$ (100). Anal. calcd. for $C_{23}H_{29}N_5O_2S$, %: C, 62.84; H, 6.65; N, 15.93. Found, %: C, 62.54; H, 6.96; N, 15.70.

***N-(2,5-Dimethyl-1H-pyrrol-1-yl)-3-{[2-({2-[(2,5-dimethyl-1H-pyrol-1-yl)carbamoyl]ethyl}sulfanyl)phenyl]amino} propanamide* (12a).** A mixture of **3a** (0.375 g, 1.25 mmol), 2,5-hexanedione (0.74 g, 6.5 mmol), 2-propanol (8 ml), and acetic acid (3 ml) was heated under reflux for 5 h. The reaction mixture was cooled to room temperature and poured to cold water (150 ml). The precipitate was filtered off and washed with water. Yield 0.44 g (78%). M. p. 105–106.5 °C. ^{1}H NMR (DMSO-d_6) δ: 1.95 (s, 6H, 2", 5"-CH_3); 1.99 (s, 6H, 2', 5'-CH_3); 2.49 (t, overlaps with DMSO-d_6, 2H, 12-CH_2); 2.62 (t, 2H, *J* = 6.5 Hz, 9-CH_2); 2.94 (t, 2H, *J* = 6.9 Hz, 11-CH_2); 3.50 (q, 2H, *J* = 6.4 Hz, 8-CH_2); 5.59 (t, 1H, *J* = 6.1 Hz, NH); 5.57–5.69 (m, 4H, 3", 4", 3', 4'-CH); 6.62 (dt, 1H, *J* = 1.1 Hz, *J* = 7.4 Hz, 5-H_{ar}); 6.74 (dd, 1H, *J* = 0.7 Hz, *J* = 8.2 Hz, 3-H_{ar}); 7.23 (t, 1H, *J* = 7.1 Hz, 4-H_{ar}); 7.39 (dd, 1H, *J* = 1.6 Hz, *J* = 7.6 Hz, 6-H_{ar}); 10.67, 10.69 (2 s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 10.92 ((C-2", C-5")-CH_3); 11.03 ((C-2', C-5')-CH_3); 29.36 (C-11); 32.88 (C-12); 33.10 (C-9); 39.22 (C-8); 102.89 (C-3", C-4', C-3', C-4'); 110.13 (C-3); 116.07 (C-1); 116.36 (C-5); 126.66 (C-2", C-5"); 126.71 (C-2', C-5'); 130.19 (C-4); 135.87 (C-6); 148.49 (C-2); 169.88 (C-13); 170.41 (C-10). MS (CI, 20 V), *m/z* (%):476.3 [M+Na]$^+$ (100), 454.3 [M]$^+$ (70). Anal. calcd. for $C_{24}H_{31}N_5O_2S$, %: C, 63.55; H, 6.89; N, 15.44. Found, %: C, 63.82; H, 6.91; N, 15.46.

***N-(2,5-Dimethyl-1H-pyrrol-1-yl)-3-{[2-({2-[(2,5-dimethyl-1H-pyrol-1-yl)carbamoyl]ethyl}sulfanyl)-4-methylphenyl] amino}propanamide* (12b)** was prepared from dihydrazide **3b** (0.311 g, 1 mmol), 2,5-hexanedione (0.74 g, 6.5 mmol), 2-propanol (8 ml), and acetic acid (2 ml) according to **12a** synthesis procedure. Yield 0.39 g (83%). M. p. 137–238 °C. ^{1}H NMR (DMSO-d_6) δ: 1.96 (s, 6H, 2", 5"-CH_3); 1.99 (s, 6H, 2', 5'-CH_3); 2.19 (s, 3H, 5-CH_3); 2.45 (t, overlaps with DMSO-d_6, 2H, 12-CH_2); 2.60 (t, 2H, *J* = 6.6 Hz, 9-CH_2); 2.94 (t, 2H, *J* = 6.7 Hz, 11-CH_2); 3.46 (t, 2H, *J* = 6.0 Hz, 8-CH_2); 5.34 (br. s, 1H, 7-NH); 5.63 (s, 4H, 3", 4", 3', 4'-CH); 6.66 (d, 1H, *J* = 8.4 Hz, 3-H_{ar}); 7.05 (d, 1H, *J* = 8.4 Hz, 4-H_{ar}); 7.21 (s, 1H, 6-H_{ar}); 10.68 (s, 2H, 13, 10-CONH). ^{13}C NMR (DMSO-d_6) δ: 10.93 ((C-2", C-5")-CH_3); 11.04 ((C-2', C-5')-CH_3); 19.81 (5-CH_3); 29.30 (C-11); 32.90 (C-12); 33.08 (C-9); 39.77 (C-8); 102.90 (C-3", C-4", C-3', C-4'); 110.38 (C-3); 116.09 (C-1); 125.00 (C-5); 126.71 (C-2", C-5", C-2', C-5'); 130.70 (C-4); 136.10 (C-6); 146.30 (C-2); 169.89 (C-13); 170.44 (C-10). MS (CI, 20 V), *m/z* (%): 490.3 [M+Na]$^+$ (100), 468.4 [M]$^+$ (30). Anal. calcd. for $C_{25}H_{33}N_5O_2S$, %: C, 64.21; H, 7.11; N, 14.98. Found, %: C, 64.41; H, 7.33; N, 15.23.

CONCLUSIONS

3-[(2-{(2-(Hydrazinocarbonyl)ethyl]sulfanyl}phenyl)amino] propanehydrazide derivatives have been synthesized and characterized using elemental analysis, mass spectrometry, and ^{1}H, ^{13}C NMR spectroscopy. All S-side chain atoms are more shielded as compared with NH ones. Compounds **4–10** possessing *ortho*-NH/S-substituted benzene with identical substituents, which contain amide and azomethine groups, can exist as mixtures of sixteen inseparable isomers in solutions; consequently, the analysis of NMR spectra is especially complicated. There was no correlation among the total steric energy values obtained for models of isomers and the NMR data; therefore it was impossible to detect the predominant isomers.

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3-[(2-{(2-(HIDRAZINOKARBONIL)ETIL]SULFANIL}FENIL)AMINO]PROPANHIDRAZIDŲ DARINIŲ SINTEZĖ IR APIBŪDINIMAS

S a n t r a u k a

Straipsnyje aprašyta naujų 3-[(2-{(2-(hidrazinokarbonil)etil]sulfanil}fenil)amino]propanhidrazidų darinių, turinčių *orto*-NH/S-pavaduotą benzeno žiedą, sintezė. Jų struktūra įrodyta elementinės analizės, masių spektrometrijos ir BMR spektroskopijos metodais. Dėl dviejų izomerijos centrų, esančių vienodai pakeistose šoninėse grandinėse, šie junginiai tirpaluose galėtų sudaryti šešiolika izomerų, tačiau BMR spektruose atsispindi tik kai kurių jų buvimas. Teoriškai galimų izomerų gausa bei koreliacijos tarp izomerų molekulių modelių suminių energijų verčių bei BMR spektrų duomenų nebuvimas apsunkina šio tipo junginių struktūros tyrimus.