Synthesis and NMR Spectroscopy Studies of Allylsulfanyl-N^1-alkyl-N^4-phenyl-1,4-phenylenediamines and their Cyclization Products, 2,3-Dihydro-1-benzothiophenes and Thiochromans

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Regioselective addition of allylmercaptan at the C-3 position adjacent to the nitrogen carrying phenyl group of the 1,4-phenylenediamine moiety of **1**−**4** was rigorously confirmed by the 1D NOE difference in combination with gHMBC experiments. The structures of 1,4-phenylenediamines **1**−**4**, allylsulfanyl-N^1-alkyl-N^4-phenyl-1,4-phenylenediamines **5**−**8**, and cyclization products **9**−**14** were completely analyzed in both $CDCl_3$ and DMSO-d_6 solutions. The ^1H and ^{13}C NMR spectra of **10** and **11** containing two chiral centers exhibit duplication for several signals indicating the existence of two diastereomeric forms. The full structures of **5** and **9** were unambiguously confirmed by X-ray crystallography. The ^1H and ^{13}C NMR spectra of all compounds were assigned using one and two-dimensional NMR techniques (APT, DEPT, 1D NOE difference, COSY, NOESY, HETCOR, gHMQC and gHMBC).

KEYWORDS: NMR, 1D NOE, gHMBC, diastereomer, 2,3-dihydrobenzothiophenes

INTRODUCTION

N^1-(Alkyl)-N^4-phenyl-1,4-phenylenediamines, such as N^1-isopropyl-N^4-phenyl-1,4-phenylenediamine (IPPD), N^1-(4-methyl-2-pentyl)-N^4-phenyl-1,4-phenylenediamine (DMBPPD), and N^1-(2-octyl)-N^4-phenyl-1,4-phenylenediamine (OPPD), have been used as antioxidants in rubber products.[1a-c] These compounds commonly display sensitizing properties,[2a-b] and have been associated with contact dermatitis.[3a-d] OPPD was reportedly added to tire sidewalls primarily to make them resistant to ozone.[4a-b]

The importance and utility of 1,4-phenylenediamines[2b] led us to study approaches to thio-substituted derivatives[5a] and cyclized analogs.[5b] Most of this work involved addition of mercapto compounds to an N^1- alkyl-N^4-aryl-*p*-quinonediimine **B**, which could lead to regioisomers **A**, or **C** (Scheme 1). Michael additions of thiols are well studied.[6a-c]

Insert Scheme 1 here

Experimentally, we found that in almost all cases, a single isomer predominated for the product and this was considered to be regioisomer **A**.[5a-b] Later work disclosed a considerably more complex picture: whereas heterocyclic thiones (tautomeric with heterocyclic thiols) indeed give regioisomers **A**,[7] most alkylthiols form regioisomers **C**[7,8] as demonstrated by 1D (NOE difference, coupled ^{13}C NMR spectra, APT and DEPT) and 2D NMR techniques (DQCOSY, NOESY, HETCOR, and heteronuclear multiple bond coherence HMBC).[7-8] Specifically, the incorrect structures given in references 5a and 5b have been corrected in references 7 and 8.

Thiol adducts of quinonediimines derived from certain functionalized thiols, e.g. methyl 3-mercaptopropionate and mercaptopropionic acid, could cyclize in the pattern of C3-C4-N4 **II** and C1-C2-N1 **III** (Scheme 2). Several representative examples have

already been examined and their structures[8] fairly established by 2D NMR techniques such as gHMQC, gHMBC.

Insert Scheme 2 here

In the present paper, we extend this work and report the synthesis of allylsulfanyl-N^1-phenyl-1,4-phenylenediamines **5**−**8** and their thermal cyclization products **9**−**12** involving C2 and C3 atoms of the 1,4-phenylenediamine moiety (Scheme 2, **IV**). Structure elucidation of **1**−**14** was achieved using gradient selected experiments. In several cases, COSY, NOESY and HETCOR (without gradients) experiments were used.

RESULTS AND DISCUSSION

Reaction of N^1-alkyl-N^4-phenyl-1,4-phenylenediamines **1**−**4** with silver oxide and magnesium sulfate in toluene at room temperature led to the formation of the corresponding phenylenediimines, which in situ reacted with allyl mercaptan in ethanol at 25 ^{o}C to afford allylsulfanyl-N^4-phenyl-1,4-phenylenediamines **5**−**8** in 60–70% yields. Regioselective addition of the S-allyl group at the C-3 position (not at C-2 position) of the 1,4-phenylenediamine moiety was rigorously confirmed by 1D NOE difference spectra in combination with gHMBC experiments. Thermal cyclizations of **5**−**8** under nitrogen at 150 ^{o}C resulted in the formation of 2,3-dihydro-1-benzothiophenes **9**−**12**, in the two cases in admixture with 3,4-dihydro-2*H*-thiochromans **13** and **14** (Scheme 3).

Insert Scheme 3 here

The formation of the cyclized products **9**–**14** involvs a thio-Claisen rearrangement as the first step followed by Markovnikov and anti-Markovnikov addition of SH to the double bond.

^{1}H NMR spectra of N^{1}-alkyl-N^{4}-phenyl-1,4 –phenylenediamines 1–4

Complete analysis of the ^{1}H NMR spectra of **1**–**4** was achieved in $CDCl_3$ and DMSO-d_6 solutions using 1D NOE difference and COSY experiments. The ^{1}H NMR assignments are given in Table 1 (numbering of atoms does not correspond to IUPAC nomenclature).

Insert Table 1 here

In the ^{1}H NMR spectra of **1**–**4** in $CDCl_3$ solution the H-2/H-6 and H-3/H-5 resonances exhibit AB type doublets ($^{3}J_{2,3} = {}^{3}J_{5,6} = 9$ Hz) at *ca* δ 6.54 and at *ca* δ = 6.89 respectively. This was further confirmed by the assignments of proton chemical shifts based on a series of NOE difference experiments: thus, the following nOe's were observed when 1-NH (at δ = 3.23−3.32) and 4-NH (at δ = 5.29–5.36) resonances were irradiated: from 1-NH to H-2/H-6 at *ca* δ = 6.54 and from 4-NH to H-3/H-5 at δ = 6.89 and to multiplets of ortho N^{4}-phenyl protons centered at δ = 6.81.

Compound **4** shows the expected conformational behavior for the cyclohexyl moiety, which exists in a chair conformation, with the bulkier group (1,4-phenylenediamine), occupying the equatorial position, i.e. the H-8 in **4** is axial (Scheme 4). Similar behavior for the cyclohexyl moiety was documented for cyclohexyl amines.[9]

Insert Scheme 4 here

^{13}C NMR spectra of 1−4

Carbon-13 chemical shift assignments of **1**–**4** in both $CDCl_3$ and DMSO-d_6 solutions experiments are summarized in Table 2.

Insert Table 2 here

In the ^{13}C NMR spectra of **1**−**4** the C-3/C-5 resonances appears in relatively downfield positions, at δ = 124.0, compared to C-2/C-6 (at δ = 114.0). Distinction between two

quaternary carbons (C-1 and C-4) in **1**–**4** was supported by strong three bond HMBC correlations from H-2/H-6 to C-4 at *ca* δ = 132.0 and from H-3/H-5 to C-1 at δ = 144.0

^{1}H NMR spectra of 3- allylsulfanyl-N^1-alkyl-N^4-phenyl-1,4 –phenylenediamines 5−8

The assigned proton chemical shifts of **5**−**8** (in both $CDCl_3$ and DMSO-d_6) are given in Table 3.

Insert Table 3 here

A characteristic coupling constant of the 1,4-phenylenediamine moieties in the range *ca* 2.5–2.8 Hz ($^4J_{2,6}$) attributable to *meta* coupled proton pairs as in substituted benzenes is assigned to H-2 resonances in the range δ 6.53–6.54 (DMSO-d_6). The doublets in the range δ 6.87–6.93 with a ^3J of 8.5 Hz belong to H-5 resonances. The measured values of 8.5 Hz (^3J) and 2.6 Hz (^4J) is close to published ^{1}H NMR data for trisubstituted benzenes in the range 8.4–9.0 Hz (^3J) and 1.7–3.0 Hz (^4J).[10a-b]

The structure of **5** was unambiguously confirmed by X-ray crystallography (Fig. 1).

Insert Figure 1 here

The assignments of S-allyl protons designated a, b, c, d (Table 3, for designation of allyl protons see Scheme 5) were based on COSY correlations and also on the magnitude of ^3J (*cis* or *trans*) coupling constants.

Analysis of coupling constants ($^2J_{ab}$, $^3J_{cd}$, $^3J_{trans}$, $^3J_{cis}$) was performed using simulation spectra. It seems that multiplicity of geminal coupled H^a and H^b resonances can not be analyzed as first order spectra in $CDCl_3$ solutions because of superpositions of several transitions for lines of H^a and H^b ($\Delta\nu/J \approx 1$). Sequences of double irradiation experiments were used for the determination of coupling constants. Experimentally determined

chemical shifts and coupling constants of H^a and H^b were examined using simulation spectra.

In the ^{1}H NMR spectra of **5**–**8** recorded in $CDCl_3$ solution, the signal at δ 4.99 (doublet of doublet of doublets, $^3J_{ac}$ = 16.9, $^2J_{ab} \approx 1.0$ and $^4J_{ad} \approx 1.4$) was assigned to H^a and the relatively high frequency doublet of doublets of triplets (ddt, $^3J_{ca}$ = 16.9, $^3J_{cb}$ = 10.0, $^3J_{cd}$ = 6.8 Hz) was assigned to H^c. The portion of ^{1}H NMR spectrum (Fig. 2) of 8 for the allylic protons is given as representative example.

Insert Figure 2 here

In contrast to the ^{1}H NMR spectra of **5**–**8** recorded in $CDCl_3$ solution the ^{1}H NMR spectra of **5**–**8** in DMSO-d_6 solutions for the allyl protons gave $ABMX_2$ type spectra, where the AB part is related to the H^a and H^b and MX_2 to protons H^c and SCH_2. Coupling through two bonds by 1.0 Hz is close to the published values of ^2J for 2-substituted propenes[11] and 1-substituted 2-methylpropenes.[12a-d] The allylic coupling constant ($^4J_{ad}$ and $^4J_{bd}$) does change considerably with the introduction of different substituents at 1-NH. The measured values of coupling constants are listed in Table 5.

The observed coupling constant for protons on adjacent trigonal (H^c) and tetrahedral carbons, $^3J(H^c, SCH_2)$ depends on conformation giving a value near 7.0 Hz when these protons are trans oriented. The long-range allylic coupling constants also depend on the rotational conformation having the smallest value when allylic proton and the $=CH_2$ group are eclipsed. Introduction of a bulkier 1,4-phenylene group increases the populations of forms *i*) and *ii*) at the expense of *iii*). The value of 7.1 Hz between H^c and SCH_2 protons is in good agreement with published data for the same coupling constants

in several olefins.[11,12a-d] Stable conformations for S-allyl substituents are illustrated in Scheme 5.

Insert Scheme 5 here

^{13}C NMR spectra of 5–8

The assigned carbon-13 chemical shifts of **5**–**8** are summarized in Table 4.

Insert Table 4 here

Long-range HMBC correlations through three bonds (^3J) between 4-NH and C-3 (quaternary carbon) in the range *ca* δ = 134.0 and C-5 at δ = 127.0 (protonated carbon) unambiguously confirmed addition of the allylsulfanyl group at the C-3 position of 1,4-phenylenediamine moiety. Distinction of chemical shifts of quaternary carbons C-1 and C^{ipso}/Ph was made on the basis of HMBC cross peaks. The contour plot of gHMBC spectra of **5**–**8** (in DMSO-d_6 solution) displayed three bond cross peaks between C^{meta}/Ph and C^{ipso}/Ph in the range δ = 145.28–147.81 and between C<u>H</u>N^1 and C-1 of the 1,4-phenylediamine moiety in the range δ = 146.06–145.75. The contour plot of the gHMBC spectra revealed for H-2 and H-6 protons show strong three bond correlations to the carbon signal at *ca* δ = 128.0, which was assigned definitively to C-4. The gHMBC cross peaks through three bonds between H-5 and a carbon signal at δ = 134.0 and also between the SCH_2 and a carbon signal at δ = 134.0 confirmed unambiguously the assignment of C-3.

The assigned chemical shifts values of the N^1-alkyl groups for **5**–**8**, in particular assignments of C-3 and C-5 resonances, were based on three bond correlations between 6-CH_3 and C-5 (δ = 31.34) and between H-1 and C-3 (δ = 28.84) in **7** for the 2-octyl group is similar to published ^{13}C NMR data for acyclic aliphatic amines.[13]

^{1}H NMR spectra of N^4-(alkyl)-2-methyl-N^7 phenyl-2,3-dihydro-1-benzothiophene-4,7-diamines 9–12

The assigned ^{1}H NMR data for compounds **9**−**12** are listed in Table 5.

Insert Table 5 here

For assignment of the protons in **9**, a series of 1D NOE difference experiments was performed (Fig. 3). The assignments of H-3β/H-2β, 2-CH_3 and H-3α were initially based on the magnitude of the vicinal coupling constant observed in the five-membered ring.[14] In these sulfur and nitrogen containing compounds, the trans vicinal coupling was smaller than the *cis* vicinal coupling. In the ^{1}H NMR spectrum of **9** recorded in DMSO-d_6 solution the H-3α resonance appears in a relatively low frequency region at δ = 2.79 compared to H-3β (δ = 3.25). The established assignments were supported by a sequence of NOE experiments. Irradiation of the 2-CH_3 resonance at δ = 1.44 resulted in nOe enhancements for protons at δ = 2.79 (H-3α) and H-2 at δ = 3.89 (Fig. 2c). The nOe's also were observed between H-2β at δ = 3.89 and H-3β at δ = 3.25 and 2-CH_3 (δ = 1.33) when H-2β was irradiated. The nOe effects from H-9 (δ = 3.54) and 7-NH (δ 7.04) to protons H-5 at δ = 6.30 and H-6 at δ 6.80 respectively are conclusive (Fig. 3d and 3g).

Insert Figure 3 here

The full structure of **9** was unambiguously determined by single crystal X-ray crystallography. It crystallizes in the triclinic space group P-1, again with two molecules in the asymmetric unit, each of which has the five membered ring disordered with the methyl group in two positions (Fig. 4).

Insert Figure 4 here

In the ^{1}H NMR spectrum of **9** in $CDCl_3$ solution, the H-3 protons appear as doublets of doublets of doublets (ddd) at δ 2.75 and δ 3.22 ($^{2}J_{3\alpha,3\beta}$ = 14.9, $^{3}J_{3\alpha,2\beta}$ = 7.9 and $^{6}J_{3\beta,6} \approx {}^{6}J_{3\alpha,6} \approx$ 0.7 Hz). To confirm the long-range coupling constant through six bonds (^{6}J) a long-range COSY experiment was run with 200 ms mixing time. The contour plot of the COSY spectrum of **9** revealed off diagonal cross peaks for both H-3 protons at δ = 2.75 and δ = 3.22 respectively, proving couplings to H-6 (δ = 2.75).

The ^{1}H NMR spectral characterization of the diastereomeric forms of 10 and 11

Compounds **10** and **11** containing two chiral centers exhibit in their ^{1}H and ^{13}C NMR spectra doubling of several signals, indicating the presence of two diastereomeric forms. In fact, the relative configuration of methyl substituents at C-2 in the benzothiophene moiety and at C-9 of the alkyl moieties was impossible to be determined.

However, each diastereomer can be partially characterized by ^{1}H and ^{13}C NMR data. Both diastereomeric forms I and II show nonequivalence for the 2-methyl, methylene (3-CH_2 and 10-CH_2), 11-CH_3^A and 11-CH_3^B and 4-NH in their ^{1}H NMR spectra (Table 5). The ^{1}H NMR spectrum of **10** for the methyl region in $CDCl_3$ is shown in Fig. 5.

Insert Figure 5 here

Similarly to **9**, the H-3 protons in **10** and **11** show long-range coupling of *ca* 0.7 Hz via six bonds to H-6 at δ = 6.82 and δ = 6.80 respectively. A series of double resonance and long-range COSY experiments for **10** were performed to confirm spin-spin interaction between H-3α (or H-3β) and H-5 and H-6 of the benzothiophene moiety (Fig. 6).

Insert Figure 6 here

The pair of chemical shifts for H-3 at δ = 2.75/δ 2.82 and at δ = 3.23/δ 3.29 in **10** and at δ = 2.76/2.82 and at δ = 3.23/3.27 in **11** (see Table 5) clearly show the presence of two diastereomers (I and II) for both compounds.

The values of geminal coupling constants of 15.8 Hz between geminal coupled H-3 protons, and vicinal coupling of 6.6 Hz between cis oriented H-3β and H-2β and transoid *vicinal* coupling of 7.9 Hz between H-3α and H-2β for both compounds **10** and **11** are the same.

^{13}C NMR spectra of 9–12

The assigned carbon-13 chemical shifts (in both $CDCl_3$ and DMSO-d_6) of **9**–**12** are listed in Table 6.

Insert Tables 6 here

In contour plots of HMBC spectra of **9**–**12** the H-2 signals show two bond correlations to C-3 at δ ≈ 42.0 and three bond correlations to two quaternary carbons C-3a and C-7a at δ ≈ 124.0 and at δ ≈ 138.0, respectively. Assignments of C-3a and C-7a were corroborated additionally, on the basis of the HMBC cross peaks between C-3a and H-5 at δ ≈ 6.36 and between C-7a and H-6 at δ ≈ 6.98. The contour plot of HMBC spectra of **9**−**12** reveals strong cross peaks between H-5 at δ ≈ 6.36 and quaternary carbon C-7 at δ ≈ 126.0, strong cross peaks were observed between H-6 at δ ≈ 6.98 and quaternary carbon C-4 at δ ≈ 141.0. The C-5 (at δ ≈ 108.0) and C-6 (δ ≈ 123.86–123.90) resonances were assigned on the basis of one bond-heterocorrelation peaks observed in contour plots of gHMQC spectra in $CDCl_3$ solution. Assignments of N^1-alkyl and N^4–phenyl carbons are based on one-bond HMQC correlations.

^{1}H NMR spectra of N^{5}-(isopropyl)-N^{8}-phenyl-5,8-thiochromanediamine 13 and N^{5}-(cyclohexyl)-N^{8}-phenyl-5,8-thiochromanediamine 14

The assigned proton chemical shifts of **13** and **14** are given in Table 7.

Insert Table 7 here

^{1}H NMR chemical shift values are similar to those of **9**−**12**. The relatively high field region at δ = 6.35 and at δ = 6.36 were assigned to H-6. For **13** and **14**, the H-7 resonances appear at δ = 6.81 and at δ = 6.80, respectively. In the ^{1}H NMR spectra of **13** and **14** the sulfur containing six membered ring protons exhibit multiplets centered at δ = 2.00 and at δ = 2.80, which were assigned to H-3 and H-4. For both compounds, H-2 appears as a triplet δ = 2.48 and δ = 2.47 with a coupling constant of 6.3 Hz. Connectivity of H-2, H-3 and H-4 was based on three bond COSY correlations and was supported by selective irradiation experiments.

^{13}C NMR spectra of 13 and 14

The assigned carbon-13 chemical shifts of **13** and **14** in both $CDCl_3$ and DMSO-d_6 solutions data are given in Table 8.

Insert Table 8 here

The SCH_2 protons of **13** and **14** at δ = 2.48 and δ = 2.47 respectively are correlated with the directly bound carbon resonances at δ = 23.37 and δ = 23.35. These protons also show long-range coupling to a methylene carbon at δ = 25.40 (C-4 of **13**), δ = 25.61 (C-4 of **14**) and quaternary carbons at δ = 132.12 (in **13**) and δ = 132.18 (in **14**). The H-3 (δ = 1.98–2.04 and δ = 1.99–2.04) show long-range coupling through three bonds to a quaternary carbon, C-4a, at δ = 118.45 and δ = 118.30. Assignments of quaternary carbons C-4a and C-8a in **13** were additionally confirmed by examining the three bond

couplings from H-6 (δ = 6.35) and H-7 (δ = 6.81) protons. Both quaternary carbons (C-4a and C-8a) in **14** exhibit cross peaks in the contour plot of the HMBC spectrum due to long-range coupling to the H-6 and H-7 protons at δ = 6.36 and δ = 6.80 respectively.

In solving the resonance assignments of quaternary carbons C-5 and C-8 the long-range correlations between H-6 (δ = 6.35) and C-8 at δ = 126.72 and between the H-9 at δ = 3.57 and quaternary carbon, C-5 at δ = 143.39 are conclusive. The SCH_2 show long-range correlations in **14** between H-6 (δ = 6.36) and quaternary carbon, C-8 at δ = 126.76 and between a multiplet centered at δ = 3.28 and a quaternary carbon, C-5, at δ = 143.16.

CONCLUSION

1D NOE difference experiments in combination with gHMBC experiments confirmed the regioselective addition of allyl mercaptan to the 3-position of the 1,4-phenylenediamine moiety of **1**−**4**. The structure of **5** as a representative example of **5**−**8** was confirmed by X-ray crystallography. Further we established using 2D NMR techniques the structures of cyclized products **9**–**14**. The structure of **9** additionally was confirmed by X-ray analysis. The assignments of **1**–**14** provide vital information on the chemistry of N^1-alkyl-N^4-phenyl-1,4-phenylenediamines.

EXPERIMENTAL

The 1D and 2D NMR experiments were performed using a Mercury 300 MHz (Varian) NMR machine equipped with a 5 mm PFG switchable probe. Chemical shifts are reported in ppm from tetramethylsilane (TMS) used as internal standard ($\delta_H = 0$).

The ^{1}H NMR spectra were acquired at 298 K with 32 scans (nt), 4 KHz spectral width (sw), 32 K data points (np) in the time domain, a 4 s acquisition time (at), a 2 s relaxation

delay (d1) and 4.5 μs pulse 30^{o} pulse width (pw). The FID's were zero filled to 128 K and multiplied by Lorentz-Gauss window functions (lb = -0.5 and gb = 0.4).

The ^{13}C NMR spectra were acquired using a 5.1 μs (pulse width 30^{o}), a 1.8 s acquisition time, a spectral width of *ca* 12000 Hz and WALTZ decoupling. The FID's were zero-filled to 128 K.

For the NOE difference experiments, the NMR sample was prepared by dissolving *ca* 15 mg of a compound in 0.7 mL $CDCl_3$ in 5 mm NMR tube. The tube was purged with argon to remove dissolved oxygen for 1 min before running NOE experiments.

The COSY spectra were acquired with a spectral width of 3 KHz in F1 and F2 dimensions. A sinebell and shifted sine bell window functions was used in both dimensions. The FID's in both dimensions were zero-filled to 2048.

The NOESY spectra were recorded also with a spectral width of 3 KHz in both dimensions using 1024 x 1024 data matrix and 512 time increments of each 16 scans (mix time 0.8 s), in phase-sensitive mode, and processed with gauss apodization function.

For the HETCOR spectra, the conditions were as follows: spectral width of *ca* 12 KHz for ^{13}C and *ca* 3 KHz for ^{1}H spectra, pulse width 90^{o} (13.5 μs for ^{1}H, 15.3 μs for ^{13}C), relaxation delay 1.0 s, number of increments 256 or 512, FT size 2048x1024. The FID's were processed using sinebell functions (sb and sbs).

The gHMQC and gHMBC spectra were acquired at 25 ^{o}C on 20 mg samples in 0.7 mL $CDCl_3$ and DMSO-d_6 solutions with a 0.4 s acquisition time, 2048 data points, a 2500 Hz spectral width in F2, 10500 Hz spectral width in F1, a 15.6 μs ^{13}C 90^{o} pulse width, 32 dummy cycles, 16 scans and with 512 increments. The FID's were processed using Gaussian functions (gf and gfs) and were zero filled to 1024 x 2048 data size.

Synthesis

General procedure for the preparation of N^1-alkyl-2-(allylsulfanyl)-N^4-phenyl-1,4-benzenediamines 5–8

To a solution of N^1-alkyl-N^4-phenyl-p-phenylenediamines **1–4** (5 mmol) in toluene (30 mL) was added Ag_2O (10 mmol) and $MgSO_4$ (14 mmol) consecutively at room temperature. The resulting suspension was stirred at room temperature overnight (around 15h). After filtration (Celite) and evaporation of toluene, the residue was dissolved in ethanol (50 mL), and then allyl mercaptan (0.5 mL, 5 mmol) was added dropwise at room temperature. The final mixture was stirred at r.t for 2-22 h. Upon removal of ethanol, the residue was purified by column chromatography on silica gel (hexane/ethyl acetate, 50/1) to give N^1-alkyl-2-(allylsulfanyl)-N^4-phenyl-1,4-benzenediamines **5–8**.

3-(Allylsulfanyl)-N^1-isopropyl-N^4-phenyl-1,4-benzenediamine (5). Yellow prism, mp 60.0–61.0 ^oC (67%). Anal. Calcd for $C_{18}H_{22}N_2S$: C, 72.44; H, 7.43; N, 9.39. Found: C, 72.26; H, 7.70; N, 9.29.

3-(Allylsulfanyl)-N^1-(4-methyl-2-pentyl)-N^4-phenyl-1,4-benzenediamine (6). Yellow oil (65%). Anal. Calcd for $C_{21}H_{28}N_2S$: C, 74.07; H, 8.29; N, 8.23. Found: C, 73.98; H, 8.63; N, 8.48.

3-(Allylsulfanyl)-N^1-(2-octyl)-N^4-phenyl-1,4-benzenediamine (7). Yellow oil (68%). Anal. Calcd for $C_{23}H_{32}N_2S$: C, 74.95; H, 8.75; N, 7.60. Found: C, 74.80; H, 8.96; N, 7.70.

3-(Allylsulfanyl)-N^1-cyclohexyl-N^4-phenyl-1,4-benzenediamine (8). Yellow oil (63%). Anal. Calcd for $C_{21}H_{26}N_2S$: C, 74.51; H, 7.74; N, 8.28. Found: C, 74.85; H, 8.07; N, 8.63.

General procedure for N^4-(alkyl)-2-methyl-N^7-phenyl-2,3-dihydro-1-benzothiophene-4,7-diamines 9-12 and N^5-(isopropyl)-N^8-phenyl-5,8-thiochromanediamine 13 and N^5-(cyclohexyl)-N^8-phenyl-5,8-thiochromanediamine 14

Under nitrogen, the N^1-alkyl-2-(allylsulfanyl)-N^4-phenyl-1,4-benzenediamines **5–8** (2 mmol) was heated at 150–155 ^oC overnight. After cooling to room temperature, the reaction mixture was subject to column chromatography on silica gel by gradual elution (hexane; hexane-ethyl acetate, 50:1) to give pure products. In cases **9** and **12**, N^5-(isopropyl)-N^8-phenyl-5,8-thiochromanediamine **13** and N^5-(cyclohexyl)-N^8-phenyl-5,8-thiochromanediamine **14** were isolated as the first fraction and corresponding minor product, respectively.

N^4-Isopropyl-2-methyl-N^7-phenyl-2,3-dihydro-1-benzothiophene-4,7-diamine (9). Yellow prism, mp 76.0–78.0 ^oC (54%). Anal. Calcd for $C_{18}H_{22}N_2S$: C, 72.44; H, 7.43; N, 9.39. Found: C, 72.22; H, 7.73; N, 9.27.

2-Methyl-N^4-(4-methyl-2-pentyl)-N^7-phenyl-2,3-dihydro-1-benzothiophene-4,7-diamine (10). Yellow oil (75%). Anal. Calcd for $C_{21}H_{28}N_2S$: C, 74.07; H, 8.29; N, 8.23. Found: C, 74.11; H, 8.50; N, 8.22.

2-Methyl-N^4-(2-octyl)-N^7-phenyl-2,3-dihydro-1-benzothiophene-4,7-diamine (11). Yellow oil (65%). Anal. Calcd for $C_{23}H_{32}N_2S$: C, 74.95; H, 8.75; N, 7.60. Found: C, 75.30; H, 9.16; N, 7.62.

N^4-Cyclohexyl-2-methyl-N^7-phenyl-2,3-dihydro-1-benzothiophene-4,7-diamine (12). Yellow oil (53%). Anal. Calcd for $C_{21}H_{26}N_2S$: C, 74.51; H, 7.74; N, 8.28. Found: C, 74.83; H, 8.19; N, 8.14.

***N*^{5}-isopropyl-*N*^{8}-phenyl-5,8-thiochromanediamine (13).** White needles, mp 99.0–101.0 ^{o}C (11%). Anal. Calcd for $C_{18}H_{22}N_2S$: C, 72.44; H, 7.43; N, 9.39. Found: C, 72.69; H, 7.68; N, 9.36.

***N*^{5}-Cyclohexyl-*N*^{8}-phenyl-5,8-thiochromanediamine (14).** Yellow oil (11%). Anal. Calcd for $C_{21}H_{26}N_2S$: C, 74.51; H, 7.74; N, 8.28. Found: C, 74.60; H, 8.18; N, 8.08.

X-ray crystallography

Data were collected with a Siemens SMART CCD area detector, using graphite monochromatized MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods using SHELXS[15] and refined on F^2, using all data, by full-matrix least-squares procedures using SHELXTL.[16] Hydrogen atoms were included in calculated positions, with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbons, except for the NH hydrogens which were found in difference maps and their positions refined.

Crystal data for 5: $C_{16}H_{22}N_2S$, MW 298.44, monoclinic, $P2_1/c$, a = 25.284(3), b = 12.290(1), c = 10.931(1) Å, β = 100.430(2) ^{o}, V = 3340.6(6) Å ^{3}, Z = 8, T = -105 ^{o}C, F(000) = 1280, μ (MoKα) = 0.190 mm^{-1}, D_{calcd} = 1.187 g.cm^{-3}, $2\theta_{max}$ 45^o (CCD area detector, 99.8% completeness), wR(F^2) = 0.0663 (all 4357 data), R = 0.0346 (2356 data with I > 2σI).

Crystal data for 9: $C_{16}H_{22}N_2S$, MW 298.44, triclinic, P-1, a = 9.018(1), b = 10.739(2), c = 17.775(2) Å, α = 80.971(2), β = 81.651(2), γ = 73.782(2) ^{o}, V = 1623.1(4) Å ^{3}, Z = 4, T = -105 ^{o}C, F(000) = 640, μ (MoKα) = 0.195 mm^{-1}, D_{calcd} = 1.221 g.cm^{-3}, $2\theta_{max}$ 45^o (CCD area detector, 99.3% completeness), wR(F^2) = 0.1137 (all 4223 data), R = 0.0517 (2728 data with I > 2σI).

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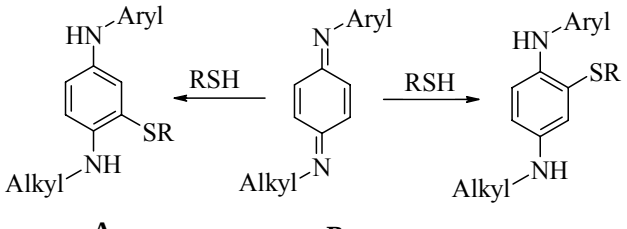
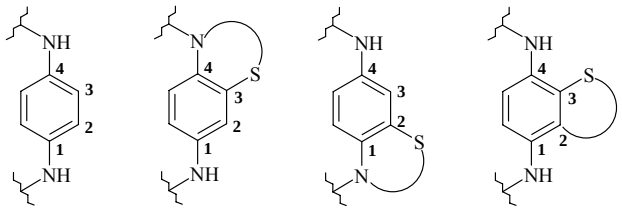
Scheme 1

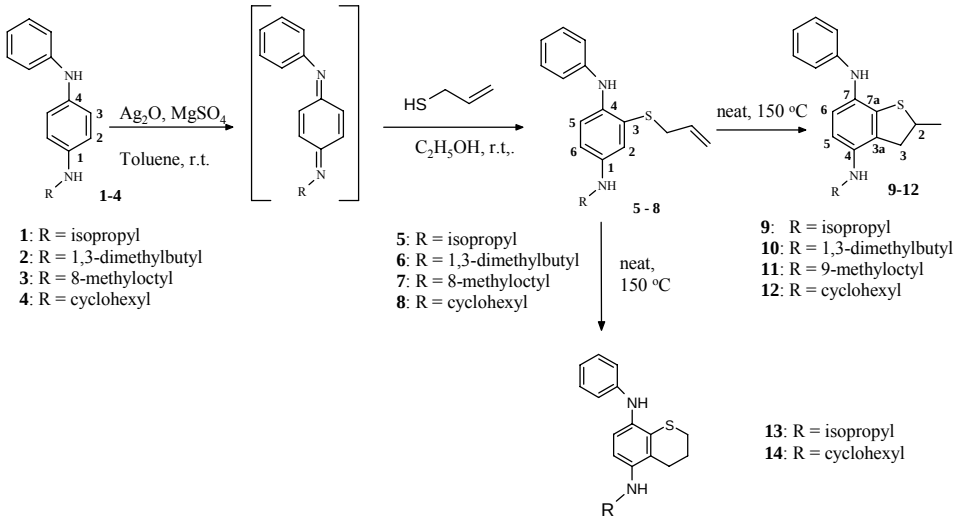


A **B** **C**

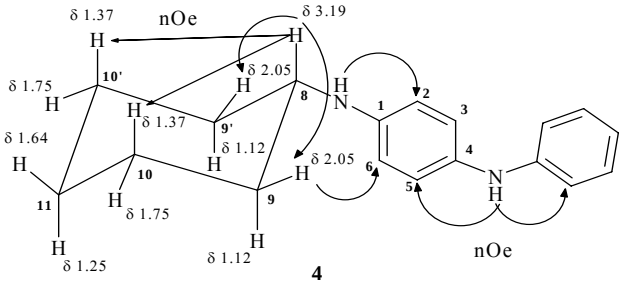
Scheme 2



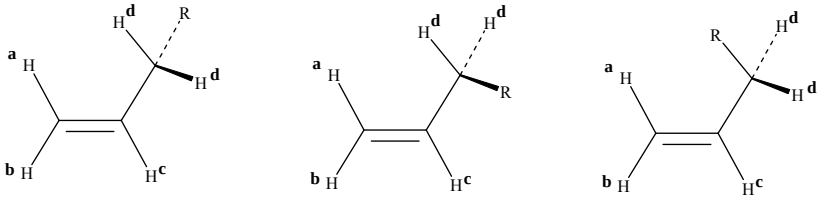
I **II** **III** **IV**



Scheme 3



Scheme 4



Scheme 5

Table 1. Proton chemical shift assignments of N^1-alkyl-N^4-phenyl-1,4-benzenediamines **1-4**

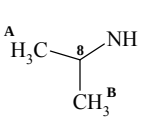
Comp	Solvent	H-2/H-6	H-3/H-5	4-NH	1-NH	H-8	8-CH_3^A	8-CH_3^B
1	$CDCl_3$	6.53 – 6.58	6.95 – 7.19	5.32	3.28	3.57	1.18	1.18
		(m)	(m)	(br s)	(br s)	(sept, 6.3)	(d, 6.3)	(d, 6.3)
	DMSO-d_6	6.52 – 6.57	6.79 – 6.99	7.46	4.96	3.48	1.12	1.12
		(m)	(m)	(br s)	(br s)	(sept, 6.4)	(d, 6.3)	(d, 6.3)
2[a]	$CDCl_3$	6.53 – 6.58	6.96 – 7.01	5.36	3.25	3.48	1.15	1.26 (dt, 13.6, 6.9)*
		(m)	(m)	(br s)	(br s)	(sext, 6.4)	(d, 6.2)	1.47 (dt, 13.6, 7.0)
	DMSO-d_6	6.49 – 6.55	6.84 – 6.89	7.46	4.95	3.38	1.06	1.19(dt, 13.4. 6.9) *
		(m)	(m)	(br s)	(br d, 8.8)	(sept, 6.6)	(d, 6.3)	1.44 (dt, 13.4, 7.0)
3[b]	$CDCl_3$	6.51 – 6.57	6.95 – 7.00	5.34	3.23	3.39	1.16	1.52 – 1.59 (m)*
		(m)	(m)	(br s)	(br s)	(sext, 6.1)	(d, 6.3)	1.37 – 1.44 (m)*
	DMSO-d_6	6.49 – 6.55	6.84 – 6.90	7.45	4.96	3.31	1.08	1.46 – 1.56 (m)*
		(m)	(m)	(br s)	(br d, 8.4)	(sept, 6.6)	(d, 6.2)	1.31 – 1.39 (m)*
4	$CDCl_3$	6.52 – 6.58	6.93 – 6.99	5.29	3.32	3.19	–	–
		(m)	(m)	(br s)	(br s)	(tt, 10.2, 3.7)		
	DMSO-d_6	6.51 – 6.55	6.84 – 6.89	7.45	5.05	3.11	–	–
		(m)	(m)	(br s)	(br s)	(unresolv m)		

N^4-Phenyl ring protons

Comp	Solvent	*ortho*/Ph	*meta*/Ph	*para*/Ph
1	$CDCl_3$	6.79 – 6.83 (m)	6.72 – 6.78 (m)	6.72 – 6.78 (m)
	DMSO-d_6	6.79 – 6.83 (m)	7.05 – 7.11 (m)	6.57 – 6.63 (m)
2	$CDCl_3$	6.79 – 6.84 (m)	7.13 – 7.20 (m)	6.72 – 6.83 (m)
	DMSO-d_6	6.74 – 6.79 (m)	7.04 – 7.11 (m)	6.56 – 6.62 (m)
3	$CDCl_3$	6.78 – 6.82 (m)	7.12 – 7.19 (m)	6.72 – 6.78 (m)
	DMSO-d_6	6.55 – 6.62 (m)	7.04 – 7.11 (m)	6.75 – 6.81 (m)
4	$CDCl_3$	6.78 – 6.82 (m)	7.11 – 7.19 (m)	6.71 – 6.77 (m)
	DMSO-d_6	6.56 – 6.62 (m)	6.75 – 6.80 (m)	7.04 – 7.11 (m)

a) **2** in $CDCl_3$: * - 9 – CH_AH_B, 1.76 (sept, 6.8, H-10), 0.91 (d, 6.6, 10-CH_3^A), 0.94 (d, 6.5, 10-CH_3^B); ***b)*** **3** in $CDCl_3$: 1.25 – 1.43 (m, 10-CH_2 + 11-CH_2 + 12-CH_2 + 13-CH_2), in DMSO-d_6: 1.18 – 1.39 (m, 10-CH_2 + 11-CH_2 + 12-CH_2 + 13-CH_2)

Table 2. Carbon-13 chemical shift assignments of N^1-alkyl-N^4-phenyl-1,4-benzenediamines **1-4**



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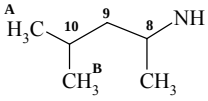

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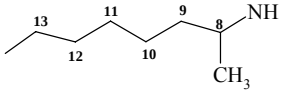

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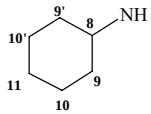


4

Comp	Solvent	C-1	C-2/ C-6	C-3/C-5	C-4	C-8	8-CH_3^A	C-9	C-10	10-CH_3^A	C-11	C-12
1[a]	$CDCl_3$	143.78	114.16	123.91	132.18	44.65	23.00	–	–	–	–	–
	DMSO-d_6	143.72	113.32	122.59	131.28	43.49	22.58	–	–	–	–	–
2[b]	$CDCl_3$	144.09	113.93	124.11	131.97	46.96	21.01	46.91	25.07	22.40	–	–
	DMSO-d_6	143.91	112.99	122.65	131.00	46.05	20.73	45.76	24.52	22.57	–	–
3[c]	$CDCl_3$	144.07	113.97	124.05	131.97	48.96	20.76	37.21	29.34	–	26.10	31.80
	DMSO-d_6	143.95	113.04	122.64	131.01	47.75	20.42	36.42	28.90	–	25.73	31.37
4	$CDCl_3$	143.68	114.05	123.98	132.02	52.16	–	33.48	24.98	–	25.87	–
	DMSO-d_6	143.58	113.10	122.66	131.03	50.99	–	32.76	24.63	–	25.26	–

N^4-phenyl ring carbons

Comp	Solvent	C^{ipso}	C^{ortho}	C^{meta}	C^{para}
1	$CDCl_3$	146.25	114.68	129.13	118.56
	DMSO-d_6	146.68	113.66	128.90	116.99
2	$CDCl_3$	146.37	114.65	129.17	118.55
	DMSO-d_6	146.67	113.56	128.82	116.85
3	$CDCl_3$	146.35	114.63	129.14	118.52
	DMSO-d_6	146.72	113.55	128.85	116.85
4	$CDCl_3$	146.30	114.61	129.11	118.49
	DMSO-d_6	146.72	113.52	128.88	116.87

a) **1** in $CDCl_3$: δ 23.0 (8-CH_3^B), in DMSO-d_6: δ 22.58 (8-CH_3^B); ***b)*** **2** in $CDCl_3$: δ 22.96 (10-CH_3^B), in DMSO-d_6: δ 22.71 (10-CH_3^B); c) **3** in $CDCl_3$: δ 22.59 (C-13), δ 14.06 (C-14) , in DMSO-d_6: δ 22.10 (C-13), δ 13.93 (C-14)

Table 3. Proton chemical shift assignments of 3-allylsulfanyl-N^1-alkyl-N^4-phenyl-1,4-benzenediamines **5-8**

Comp	Solvent	H-2	H-5	H-6	H^a	H^b	H^c	SCH_2	1-NH	4-NH
5	$CDCl_3$	6.72 (d, 2.8)	7.14 (d, 8.6)	6.49 (dd, 8.6, 2.8)	5.00 (dq, 16.9, 1.4)	4.98 (dq, 10.0, 0.8)	5.81 (ddt, 16.9, 10.0, 7.1)	3.36 (dt, 7.1, 1.1)	3.21 (br s)	6.00 (br s)
	DMSO-d_6	6.54 (d, 2.5)	6.89 (d, 8.5)	6.39 (dd, 8.5, 2.5)	5.19 (dq, 16.9, 1.5)	5.05 (dq, 10.1, 1.0)	5.82 (ddt, 16.9, 10.1, 6.8)	3.48 (dt, 6.8, 1.2)	5.31 (br s)	6.96 (br s)
6^a	$CDCl_3$	6.70 (d, 2.7)	7.13 (d, 8.6)	6.48 (dd, 8.6, 2.7)	5.05 (dq, 17.2, 1.4)	4.99 (dq, 10.1, 0.9)	5.81 (ddt, 17.2, 10.1, 7.1)	3.36 (dt, 7.1, 1.1)	3.10 (br s)	5.88 (br s)
	DMSO-d_6	6.53 (d, 2.6)	6.93 (d, 8.5)	6.38 (dd, 8.5, 2.6)	5.19 (dq, 17.0, 1.4)	5.06 (dq, 10.1, 0.9)	5.82 (ddt, 17.0, 10.1, 6.8)	3.47 (dt, 6.8, 1.0)	5.25 (br d, 8.5)	6.95 (br s)
7^b	$CDCl_3$	6.70 (d, 2.8)	7.14 (d, 8.6)	6.49 (dd, 8.6, 2.8)	5.01 (dq, 16.9, 1.4)	4.99 (dq, 10.0, 0.9)	5.82 (ddt, 16.9, 10.0, 7.2)	3.37 (dt, 7.2, 1.1)	3.26 (br s)	5.98 (br s)
	DMSO-d_6	6.53 (d, 2.5)	6.88 (d, 8.5)	6.38 (dd, 8.5, 2.5)	5.19 (dq, 16.9, 1.4)	5.05 (dq, 10.0, 0.9)	5.82 (ddt, 16.9, 10.0, 6.8)	3.47 (dt, 6.8, 0.9)	5.28 (br d, 8.1)	6.95 (br s)
8^c	$CDCl_3$	6.72 (d, 2.7)	7.13 (d, 8.6)	6.50 (dd, 8.6, 2.7)	5.01 (dq, 16.8, 1.4)	4.99 (dq, 10.0, 0.9)	5.81 (ddt, 16.8, 10.0, 7.1)	3.36 (dt, 7.1, 1.0)	3.34 (br s)	5.98 (br s)
	DMSO-d_6	6.54 (d, 2.6)	6.87 (d, 8.5)	6.39 (dd, 8.5, 2.6)	5.20 (dq, 16.9, 1.4)	5.06 (dq, 10.0, 1.0)	5.82 (ddt, 16.9, 10.1, 6.8)	3.47 (dt, 6.8, 1.1)	5.34 (br d, 7.9)	6.95 (br s)

Table 3 (continued).

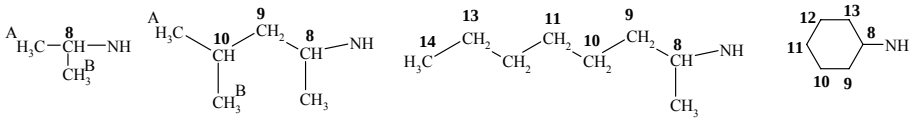
Comp	Solvent	H-8	H-9	H-10	8-CH_3	10-CH_3^A	4-CH_3^B	Phenyl ring		
								ortho	*meta*	*para*
5	$CDCl_3$	3.57 (sept, 6.2)	1.20 (d, 6.3)	–	1.20 (d, 6.3)	–	–	6.88 – 6.93 (m)	7.16 – 7.23 (m)	6.78 – 6.85 (m)
	DMSO-d_6	3.49 (sept, 6.6)	1.13 (d, 6.3)	–	1.13 (d, 6.3)	–	–	6.56 – 6.60 (m)	7.00 – 7.07 (m)	6.53 – 6.57 (m)
6	$CDCl_3$	3.46 (sext, 6.7)	1.25 (dt, 13.3, 6.9) 1.46 (dt, 13.3, 6.9)	1.75 (sept, 6.8)	1.15 (d, 6.2)	0.92 (d, 6.6)	0.94 (d, 6.6)	6.88 – 6.94 (m)	7.16 – 7.23 (m)	6.78 – 6.84 (m)
	DMSO-d_6	3.42 (sept, 6.8)	1.21 (dt, 13.3, 6.9) 1.45 (dt, 13.3, 6.9)	1.73 (sept, 6.7)	1.07 (d, 6.2)	0.87 (d, 6.6)	0.92 (d, 6.6)	6.53 – 6.59 (m)	7.01 – 7.07 (m)	6.63 – 6.59 (m)
7	$CDCl_3$	3.76 (sext, 6.7)	1.46	1.30	1.17 (d, 6.3)	–	1.36	6.88 – 6.94 (m)	7.17 – 7.24 (m)	6.79 – 6.85 (m)
	DMSO-d_6	3.29 – 3.39	–	–	1.09 (d, 6.3)	–	–	6.52 – 6.59 (m)	7.00 – 7.07 (m)	6.52 – 6.59 (m)
8	$CDCl_3$	3.19 (tt, 9.8, 3.6)	–	–	–	–	–	6.88 – 6.94 (m)	7.16 – 7.23 (m)	6.78 – 6.84 (m)
	DMSO-d_6	3.09 – 3.20 (unres m)	–	–	–	–	–	6.51 – 6.56 (m)	7.00 – 7.07 (m)	6.52 – 6.59 (m)

a) **7** in $CDCl_3$: δ 1.46 (H-2); δ 1.30 (H-3); δ 1.36 (H-4); δ 1.28 (H-5); 1.31 (H-6); DMSO-d_6: 0.86 (t, 7-CH_3); 1.45 - 1.58 (m, H-2), 1.18 - 1.42 (unres m, H-3 + H-4 + H-5 + H-6); ***b)*** **8** in DMSO-d_6: 1.89 - 1.97 (m, H-6eq + H-2eq); 1.68 – 1.76 (m, H-5eq + H-4eq); 1.55 - 1.63 (m, H-3eq); 1.22 - 1.39 (m, H-3ax + H-5ax); 1.07 - 1.24 (m, H-4ax + H-6ax + H-2ax); $CDCl_3$: 2.01 - 2.09 (m, H-6eq + H-2eq); 1.72 - 1.80 (m, H-5eq + H-4eq); 1.61 - 1.69 (m, H-3eq); 1.29 - 1.44 (m, H-3ax + H-5ax); 1.07 - 1.28 (m, H-4ax + H-6ax + H-2ax).

Table 4. Carbon-13 chemical shift assignments of 3-(allylsulfanyl)-N^1-(alkyl)-N^4-phenyl-1,4-benzenediamines **5**–**8**

Comp	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C^{ipso}	C^{ortho}	C^{meta}	C^{para}
5	DMSO-d_6	145.80	111.58	133.80	128.10	127.06	110.50	147.71	113.26	128.67	116.62
	$CDCl_3$	142.95	118.43	133.64	133.64	121.71	114.32	145.18	115.90	129.19	119.51
6	DMSO-d_6	146.06	111.22	133.92	127.88	127.22	110.28	147.78	113.21	128.69	116.58
	$CDCl_3$	143.24	118.08	127.03	133.37	121.93	114.06	145.28	115.82	129.19	118.08
7	DMSO-d_6	146.07	111.29	133.87	127.89	127.16	110.37	147.78	113.22	128.67	116.58
	$CDCl_3$	143.25	118.14	127.03	133.38	121.92	114.10	145.28	115.82	129.19	119.45
8	DMSO-d_6	145.75	111.36	134.04	127.92	127.14	110.36	147.81	113.24	128.73	116.63
	$CDCl_3$	142.91	118.25	127.01	133.48	121.88	114.20	145.26	115.84	129.20	119.47

Table 4 (continued).



Comp	Solvent	SCH_2	=CH	$=CH_2$	C-8	C-9	C-10	C-11	C-12	C-13	C-14
5	$CDCl_3$	37.73	133.66	117.51	44.83	23.01	–	–	–	–	–
	DMSO-d_6	34.26	133.94	117.50	43.24	22.52	–	–	–	–	–
6[a]	$CDCl_3$	37.70	133.68	117.52	47.15	46.89	25.06	22.56	–	–	–
	DMSO-d_6	34.22	133.93	117.51	45.57	45.94	24.50	22.57	–	–	–
7[b]	$CDCl_3$	37.71	133.68	117.51	49.13	37.19	29.35	26.08	31.81	22.60	13.94
	DMSO-d_6	36.33	133.95	117.47	47.53	34.24	28.84	25.65	31.34	22.07	–
8	$CDCl_3$	37.75	133.74	117.53	52.53	33.54	25.91	25.01	25.91	33.54	–
	DMSO-d_6	34.22	134.13	117.54	50.77	32.71	32.71	25.63	24.57	32.71	–

a - δ 21.07 (8-CH_3), δ 22.97 (10-CH_3)**;** ***b*** - 20.43 (8-CH_3)

Table 5. Proton chemical shift assignments of the N^1-(alkyl)-2-methyl-N^4-phenyl-2,3-dihydrobenzothiophene-4,7-diamines **9-12**

Comp	Solvent	H-2	2-CH_3	H-3	H-5	H-6	H-9	H-10
9	$CDCl_3$	3.98	1.44	2.75 (ddd, 14.9, 6.6, 0.7)	6.36	6.98	3.61	1.22
		(sext, 7.1)	(d, 6.7)	3.22 (ddd, 14.9, 7.9, 0.7)	(d, 8.5)	(d, 8.5)	(sept, 6.3)	(d, 6.2, CH_3)
	DMSO-d_6	3.89	1.33	2.79 (dd, 15.6, 6.5)	6.30	6.80	3.54	1.16
		(sext, 3.89)	(d, 6.7)	3.25 (dd, 15.6, 7.8)	(d, 8.4)	(d, 8.4)	(sept, 6.3)	(d, 6.4, CH_3)
10	$CDCl_3$	4.00	1.45 (d, 6.8)	2.75 (ddd, 14.8, 6.8, 0.7)	6.36	6.99	3.52	1.28 (dt, 13.7, 6.9)
		(sext, 6.7)*	1.46 (d, 6.8)	2.76 (ddd, 14.8, 6.8, 0.7)	(d, 8.7)	(d, 8.7)	(sext, 6.4)	1.27 (dt, 13.7, 6.9)
				3.23 (ddd, 14.8, 7.8, 0.7)**				1.48 (dt, 13.7, 6.9
	DMSO-d_6	3.91*	1.35	2.75 (dd, 15.8, 6.6)	6.31	6.82	3.47*	1.25 (dt, 13.3, 6.7)
		(sext, 6.7)	(d, 6.7)	2.82 (dd, 15.8, 6.6)	(d, 8.4)	(d, 8.4)	(sext, 6.8)	1.23 (dt, 13.3, 6.7)
				3.23 (dd, 15.7, 7.8)				1.53 (dt, 13.3, 6.7)
				3.29 (dd, 15.7, 7.8)				
11	$CDCl_3$	3.99	1.45	2.75 (dd, 14.8, 6.6)	6.34	6.98	3.44	1.52-1.64
		(sext, 6.8)	(d, 6.8)	3.22 (dd, 14.8, 7.8)	(d, 8.6)	(d, 8.6)	(sext, 6.3)	(m, 1H)
	DMSO-d_6	3.91	1.35	2.76 (dd, 15.8, 6.6)	6.28	6.80	3.38	1.52-1.62
		(sext, 6.7)	(d, 6.7)	2.82 (dd, 15.8, 6.6)	(d, 8.7)	(d, 8.7)	(br m)	(m, 1H)
				3.23 (dd, 15.8, 7.9)				
				3.27 (dd, 15.7, 7.9)				
12	$CDCl_3$	3.99	1.44	2.76 (ddd, 14.9, 6.6, 0.7)	6.37	6.98	3.25	2.03-2.94
		(sext, 6.7)	(d, 6.8)	3.23 (ddd, 14.9, 7.9, 0.7)	(dd, 8.4, 0.7)	(dt, 8.4, 0.7)	(tt, 9.9, 3.8)	(m, 10eq+10'eq)
	DMSO-d_6	3.91	1.44	2.79 (dd, 15.7, 6.7)	6.32	6.79	3.11-3.23	1,90-1.97
		(sext, 6.6)	(d, 6.8)	3.25 (dd, 15,7, 7.9)	(d, 8.7)	(d, 8.7)	(unresm)	(m, 10eq+10'eq)

*- two set of overlapping sextets, **- two set overlapping doublet of doublets.

Table 5 (continued).

Comp	Solvents	9-CH_3	4-NH	7-NH	*ortho/Ph*	*meta/Ph*	*para/Ph*
9	$CDCl_3$	1.21 (d, 6.3)	2.81 (br s)	5.11 (br s)	6.71 – 6.78 (m)	7.11 – 7.19 (m)	6.71 – 6.78 (m)
	DMSO-d_6	1.15 (d, 6.2)	4.36 (br d, 6.6)	7.04 (br s)	6.51 – 6.58 (m)	7.12 – 7.19 (m)	6.69 – 6.78 (m)
10[a]	$CDCl_3$	1.17 and 1.18 (d, 6.2)	2.98 (br s)	5.10 (br s)	6.69 – 6.78 (m)	7.12 – 7.19 (m)	6.69 – 6.78 (m)
	DMSO-d_6	1.10 and 1.11 (d, 6.2)	4.33 and 4.34 (br d, 8.7)	7.13 (br s)	6.56 – 6.70 (m)	6.98 – 7.06 (m)	6.48 – 6.55 (m)
11[b]	$CDCl_3$	1.18 (d, 6.3)	3.01 (br s)	5.10 (br s)	6.78 – 6.88 (m)	7.11 – 7.19 (m)	6.78 – 6.88 (m)
	DMSO-d_6	1.11 (d, 6.2)	4.32 and 4.33 (br d, 8.4)	7.09 (br s)	6.50 – 6.58 (m)	7.00 – 7.06 (m)	6.50 – 6.58 (m)
12[c]	$CDCl_3$	–	3.04 (br s)	5.10 (br s)	6.72 – 6.80 (m)	7.11 – 7.19 (m)	6.72 – 6.80 (m)
	DMSO-d_6	–	4.37 (br d, 8.0)	7.11 (br s)	6.52 – 6.58 (m)	6.98 – 7.07 (m)	6.52 – 6.58 (m)

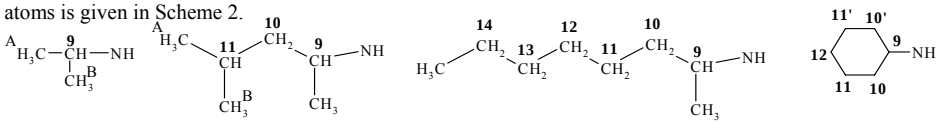
a) **10** in $CDCl_3$: δ 0.90 (d, ^3J = 6.6, 11-CH_3^A), δ 0.91 (d, ^3J = 6.3, 11-CH_3^B) and δ 0.92 (d, ^3J = 6.3, 11-CH_3^B), **10** in DMSO-d_6: δ 0.86 (d, ^3J = 6.5, 11-CH_3^A) and δ 0.87 (d, ^3J = 6.5, 11-CH_3^A), δ 0.92 (d, ^3J = 6.6, 11-CH_3^B); b***)*** **11** in $CDCl_3$: 0.89 (t, 6.9, 13-CH_3), 1.17 (d, 6.3, 9-CH_3), 1.18 (d, 6.3, 9-CH_3), 1.27 - 1.40 (unresolv multiplet, 10-$CH_A\underline{H}_B$ + 11-CH_2 + 12-CH_2+ 13-CH_2 + 14-CH_2), in DMSO-d_6: 1.23 - 1.42 (unresolv multiplet, 10-$CH_A\underline{H}_B$ + 11-CH_2 + 12-CH_2 + 13-CH_2 + 14-CH_2), 0.86 (t, 6.9, 13-CH_3), ***c)*** **12** in $CDCl_3$: 1.08 –1.28 (m, 12ax + 10ax + 10'ax), 1.28-1.41 (m, 11ax + 11'ax), 1.62 – 1.69 (m, 12eq), 1.73–1.80 (m, 11eq + 11'eq), in DMSO-d_6: 1.08 –1.39 (m, 10ax + 10'ax + 12ax + 11ax + 11'ax), 1.57–1.64 (m, 12eq), 1.68–1.75 (m, 11eq + 11eq'), 1.91 - 1.98 (m, 11eq +11'eq).

Table 6. Carbon-13 chemical shift assignments of the 2,3-dihydrobenzothiophene moiety and N^4-phenyl ring * in **9**-**12**

Comp	Solvent	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	C^{ipso}	C^{ortho}	C^{meta}	C^{para}
9	$CDCl_3$	44.34	41.50	123.98	140.67	108.55	123.79	126.48	137.75	145.77	114.71	129.07	118.68
	DMSO-d_6	43.37	41.49	125.07	141.26	107.78	125.15	123.67	138.65	147.00	113.36	128.61	116.56
10	$CDCl_3$	44.40	41.61	123.81	140.88	108.23	123.90	126.25	137.83	145.80	114.69	129.07	118.59
		44.37	41.60	–	140.86	108.21	–	–	137.80	142.90	–	–	–
	DMSO-d_6	43.45	41.59	123.54	141.51	107.41	124.83	125.34	138.84	147.10	113.36	128.67	116.55
		43.37	–	123.48	–	107.39	–	–	138.79	–	–	–	–
11	$CDCl_3$	44.40	41.58	123.81	140.86	108.37	123.88	126.25	137.78	145.78	114.67	129.05	118.57
		44.37	–	123.78	–	108.33	–	126.24	–	–	–	–	–
	DMSO-d_6	43.37	41.52	123.51	141.48	107.62	125.21	124.88	138.71	147.05	113.34	128.59	116.52
		43.33	–	123.47	–	107.55	–	124.86	–	–	–	–	–
12	$CDCl_3$	44.42	41.58	123.85	140.56	108.51	123.86	126.32	137.81	145.79	114.64	129.06	118.57
	DMSO-d_6	43.37	41.48	123.58	141.11	107.76	124.98	125.22	138.75	146.06	113.33	128.65	116.55

* - Numbering of carbon atoms is given in Scheme 2.

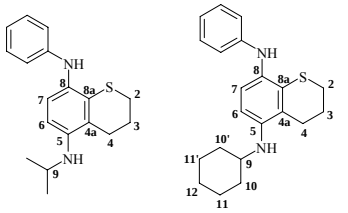
Table 6 (continued).



Comp	Solvent	2-CH_3	C-9	9-CH_3^A	9-CH_3^B	C-10	C-11	11-CH_3^A	11-CH_3^B
9	$CDCl_3$	22.37	44.50	23.16	23.21	–	–	–	–
	DMSO-d_6	22.41	43.51	22.54	22.58	–	–	–	–
10	$CDCl_3$	22.43	46.93	–	21.41	47.08	25.14	22.54	23.01
		–	46.90	–	21.37	47.06	–	22.51	22.99
	DMSO-d_6	22.43	46.91	–	21.41	47.08	25.14	22.54	23.01
		–	46.90	–	21.38	47.06	25.13	22.51	23.00
11[a]	$CDCl_3$	22.48	48.87	–	21.09	37.35	29.31	26.08*	31.79**
		22.43	–	–	21.06	37.32	–	26.07*	–
	DMSO-d_6	22.41	47.91	–	20.51	36.27	28.81	25.76*	31.31**
		22.31	47.89	–	–	–	28.80	25.74 *	–
12	$CDCl_3$	22.47	52.07	–	–	33.74	25.01	25.89	–
						33.78	24.99	(C-12)	
	DMSO-d_6	22.41	51.23	–	–	32.77	24.81	25.61	–
						32.78	24.88	(C-12)	

a) **11** in $CDCl_3$: δ 22.58 (C-14), δ 14.06 (14-CH_3); DMSO-d_6: δ 22.05 and δ 22.06 (C-14), δ 13.92 (14-CH_3). (C-12); *- (C-12), ** - (C-13).

Table 7. Proton chemical shift assignments of N^5-(isopropyl)-N^8-phenyl-5,8-thiochromanediamine and N^5-(cyclohexyl)-N^8-phenyl –5,8-thiochromanediamine **13**, **14**



Comp	Solvent	H-2	H-3	H-4	H-6	H-7	H-9	5-NH	8-NH
13[a]	$CDCl_3$	2.50	2.15-2.23	2.87-2.91	6.43	7.03	3.65	3.42	5.24
		(t, 6.3)	(m)	(m)	(d, 8.7)	(d, 8.7)	(sept, 6.2)	(br s)	(br s)
	DMSO-d_6	2.48	1.98-2.04	2.78-2.83	6.35	6.81	3.57	4.25	6.88
		(t, 6.3)	(m)	(m)	(d, 8.5)	(d, 8.5)	(unresol m)	(br s)	(br s)
14	$CDCl_3$	2.49	2.16-2.21	2.85-2.89	6.42	7.01	3.22-3.32	3.23	5.09
		(t, 6.4)	(m)	(m)	(d, 8.6)	(d, 8.6)	(unresol m)	(br s)	(br s)
	DMSO-d_6	2.47	1.99-2.04	2.78-2.81	6.36	6.80	3.18-3.28	4.20	6.87
		(t, 6.4)	(m)	(m)	(d, 8.6)	d, 8.6)	(unresol m)	(br s)	(br s)

a – in $CDCl_3$: δ 1.26 (d, ^3J = 6.2, 9-CH_3), in DMSO-d_6: δ 1.18 (d, ^3J = 6.3, 9-CH_3).

Table 7 (continued).

Comp	Solvent	10eq + 10'eq	11eq + 11'eq	12eq	*ortho*/Ph	*meta*/Ph	*para*/Ph
13	$CDCl_3$	–	–	–	6.70 – 6.77 (m)	7.13 – 7.19 (m)	6.70 – 6.77 (m)
	DMSO-d_6	–	–	–	6.50 – 6.56 (m)	6.98 – 7.05 (m)	6.50 – 6.56 (m)
14[a]	$CDCl_3$	2.04 – 2.10 (m)	1.73 – 1.80 (m)	1.64 – 1.68 (m)	6.68 – 6.71 (m)	7.11 – 7.19 (m)	6.70 – 6.76 (m)
	DMSO-d_6	1.92 – 1.98 (m)	1.68 – 1.73 (m)	1.58 – 1.63 (m)	6.49 – 6.56 (m)	6.98 – 7.04 (m)	6.49 – 6.56 (m)

a – in $CDCl_3$: δ 1.12 – 1.30 (m, 10ax + 10'ax), 1.31 – 1.42 (m, 11ax + 11'ax + 12ax), in DMSO-d_6: 1.14 – 1.36 (m, 10ax + 10'ax + 11ax + 11'ax + 12ax).

Table 8. Carbon-13 chemical shift assignments of N^5-(isopropyl)-N^8-phenyl-5,8-thiochromanediamine and N^5-(cyclohexyl)-N^8-phenyl –5,8-thiochromanediamine **13**, **14**

Comp	Solvent	C-2	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a
13	$CDCl_3$	22.04	21.61	24.55	116.31	142.79	106.29	123.88	126.91	131.02
	DMSO-d_6	23.37	22.71	25.40	118.45	143.39	106.35	124.99	126.72	132.12
14	$CDCl_3$	23.64	23.09	26.19	118.61	142.25	106.83	123.87	127.60	131.03
	DMSO-d_6	23.35	22.74	25.61	118.30	143.16	106.26	124.98	126.76	132.18
		N^8- phenyl ring				N^5-alkyl substituents				
Comp	Solvent	C^{ipso}	C^{ortho}	C^{meta}	C^{para}	C-9	9-CH_3^A	9-CH_3^B	C-11	C-12
13	$CDCl_3$	146.76	114.29	129.14	118.40	44.36	21.58	21.58	–	–
	DMSO-d_6	148.09	113.06	128.61	116.31	45.51	22.54	22.54	–	–
14	$CDCl_3$	146.71	114.17	129.07	118.29	51.78	33.62*	–	24.98	25.93
	DMSO-d_6	148.10	113.04	128.60	116.28	51.16	32.70*	–	24.78	25.39

* - (C-10)

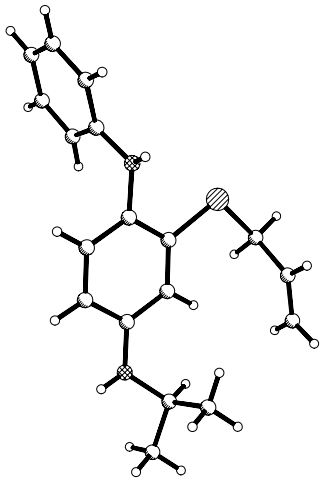


Figure 1. Perspective view of the X-ray structure of **5**.

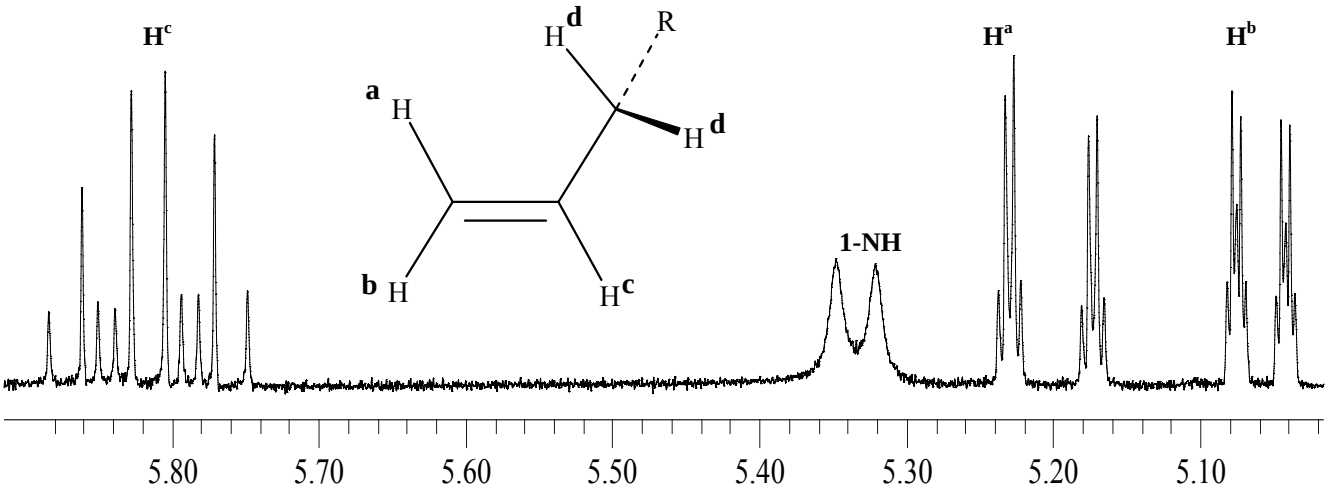


Figure 2. Expansion of the ^{1}H NMR spectrum of **8** (in DMSO-d_6) in the range of CH_2=CH-CH_2R group.

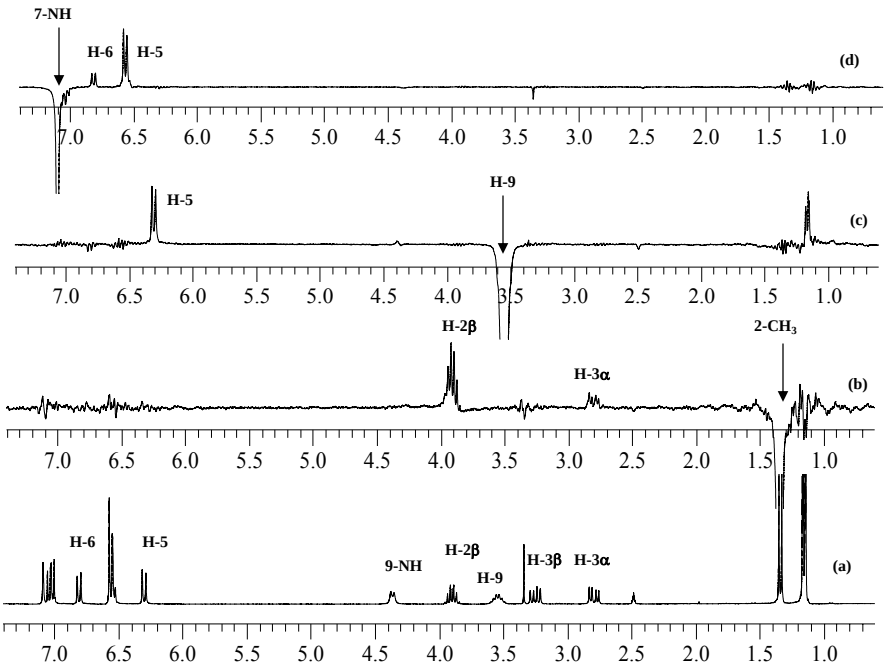


Figure 3. ^{1}H NMR spectrum **(a)** of **9** in DMSO-d_6; **(b) - (d)** NOE difference spectra; arrows indicate irradiated peaks

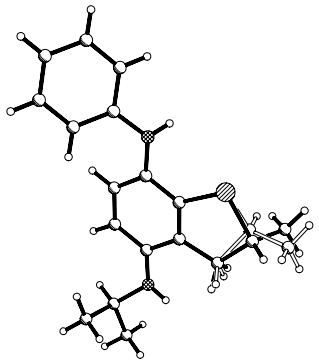


Figure 4. Perspective view of the X-ray structure of **9**, showing the disorder within the five-membered ring.

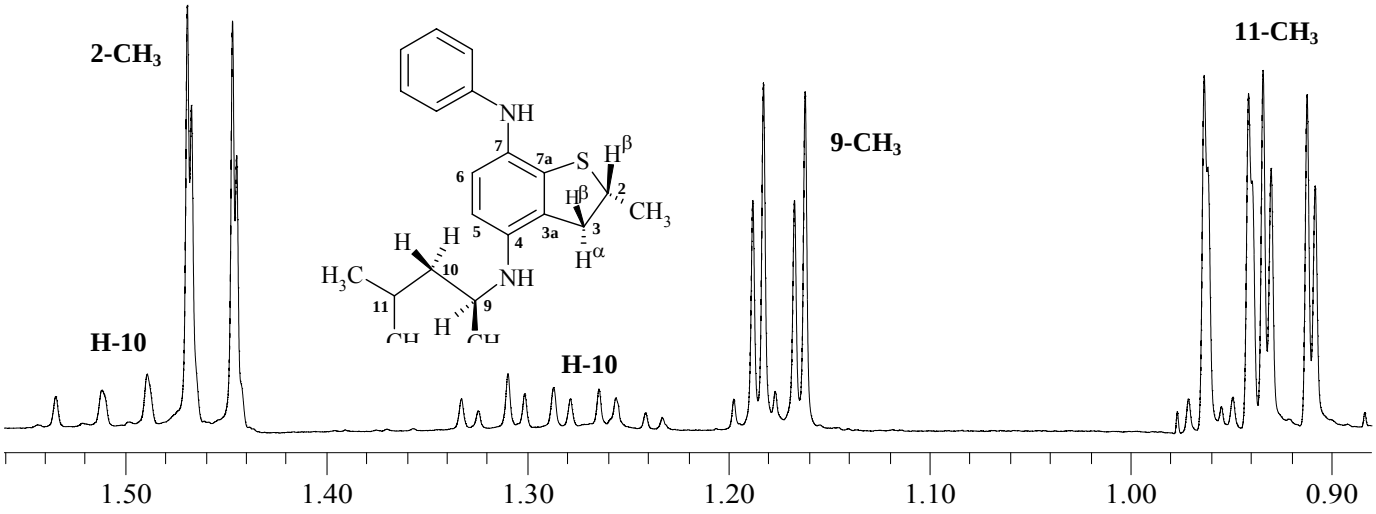


Figure 5. Methyl region of ^{1}H NMR spectrum of **10** in $CDCl_3$. (double set of 2-CH_3, 9-CH_3 and 11-CH_3 and also H-10 resonances indicate the presence of two chiral centers, at C-2 and C-9 carbon atoms, in molecule **10**. The ^{1}H NMR spectrum was processed using Lorentz/Gaussian window functions (lb = -0.5 gf = 1.6) prior to Fourier transformations and zero filled by 128 K, to get resolution-enhanced spectrum.

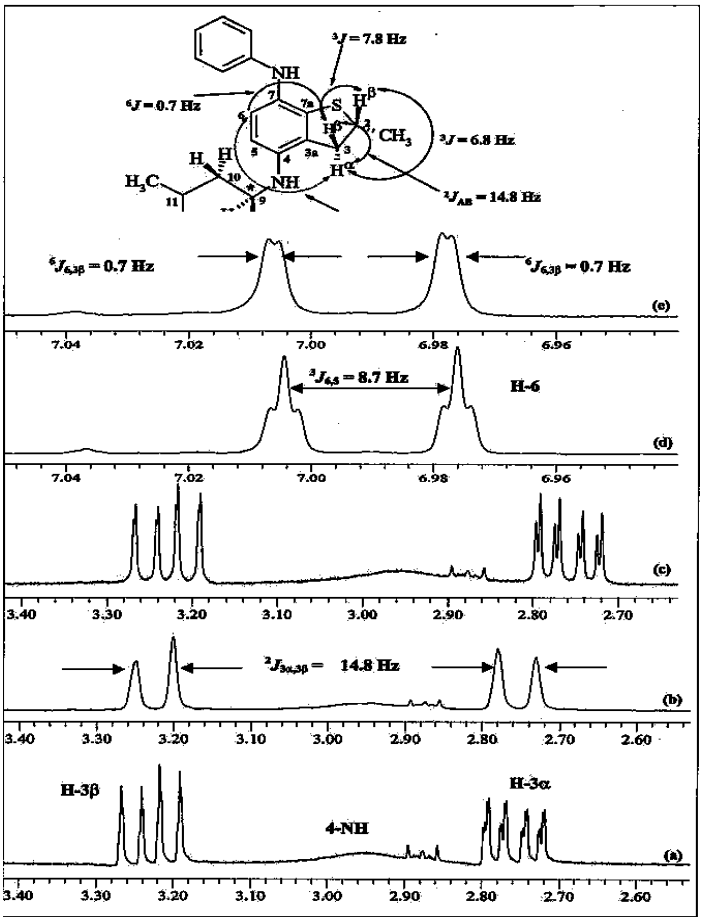


Figure 7. Portion of the ^{1}H NMR spectrum of **10** in $CDCl_3$, **(a)** without irradiation; **(b)** with irradiation of H-2 resonance at δ 4.0, for processing FID's was used line broadening function (lb = 1); **(c)** with irradiation of doublet at δ 6.99 (H-6) of the benzothiophene moiety causes two set doublet of doublets from two diastereomeric formic for H-3α and H-3β; **(d)** doublet of triplet at δ 6.99 (H-6); (e) irradiation of H-3α signal at δ .2.75.