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Synthesis of 7-Sulfonyl-Substituted Norpinan-6-ones and -thiones from 1-Bromotricyclo[4.1.0.0^{2,7}]heptane

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Abstract—1-Bromotricyclo[4.1.0.0^{2,7}]heptane reacted with benzene- and methanesulfonyl thiocyanates in benzene at 20°C via *anti* addition to the central C^1–C^7 bicyclobutane bond with formation of 6-*endo*-bromo-6-*exo*-thiocyanato-7-*syn*-(R-sulfonyl)bicyclo[3.1.1]heptanes. Treatment of the benzenesulfonyl thiocyanate adduct with potassium *tert*-butoxide in THF at 20°C gave 7-*endo*-(benzenesulfonyl)norpinan-6-one, whereas the reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene in methylene chloride afforded 7-*exo*-(benzenesulfonyl)-norpinane-6-thione which was converted into 7-*exo*-(benzenesulfonyl)norpinan-6-one by alkaline hydrolysis.

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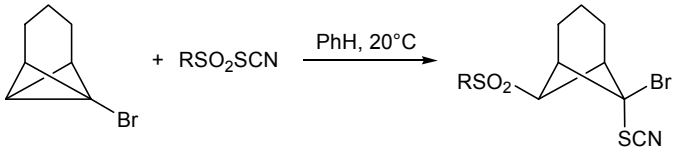
We previously reported stereoselective *anti* addition of *p*-toluene- and methanesulfonyl thiocyanates to the central C^1–C^7 bicyclobutane bond of tricyclo-[4.1.0.0^{2,7}]heptanes with formation of bicyclo[3.1.1]-heptane (norpinane) derivatives [1, 2]. While continuing studies in this line, in the present work we synthesized analogous bromo-substituted monoadducts by reaction of 1-bromotricycloheptane **1** with benzene- and methanesulfonyl thiocyanates **2a** and **2b** and examined their transformations under the action of bases.

The reactions were carried out with equimolar amounts of the reactants in benzene at 20°C for 7–8 h. In both cases, the products were the corresponding *anti*-addition products to the C^1–C^7 bond, norpinanes **3a** and **3b**, which were isolated by crystallization in 58 and 48% yield, respectively (Scheme 1).

The structure of compounds **3a** and **3b** was determined by IR and ^{1}H and ^{13}C NMR spectroscopy. The sulfonyl group in **3a** and **3b** gave rise to strong absorption bands at ~1150 and 1300 cm^{-1} in the IR spectra [3]. Stretching vibrations of the thiocyanato group were observed at ~2150 cm^{-1}, and the SCN carbon nucleus resonated in the ^{13}C NMR spectra at δ_C ~110 ppm. The norpinane skeleton of molecules **3a** and **3b** was identified by five characteristic carbon signals in the upfield region of the ^{13}C NMR spectrum [1, 2]. The *syn* orientation of the sulfonyl group on C^7 was assigned on the basis of multiplicity of the 7-H proton signal (δ ~4.1 ppm, triplet, J = 5.6 Hz) in the ^{1}H NMR spectra [4]. The configuration of C^6 followed from the chemical shift of 7-H which faces the *exo*-oriented thiocyanato group. Unambiguous proof of the structure of **3a** was obtained by X-ray analysis of its single crystal (see figure).

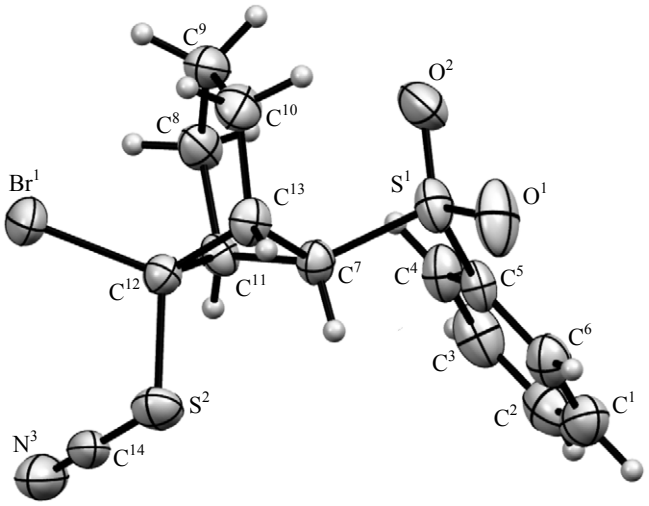
The steric structure of **3a** is characterized by almost planar trimethylene bridge, parallel orientation of one S=O bond of the sulfonyl group relative to the C^1–C^2 and C^4–C^5 bonds, and almost orthogonal orientation of

Scheme 1.



1 **2a**, **2b** **3a**, **3b**

R = Ph (**a**), Me (**b**).

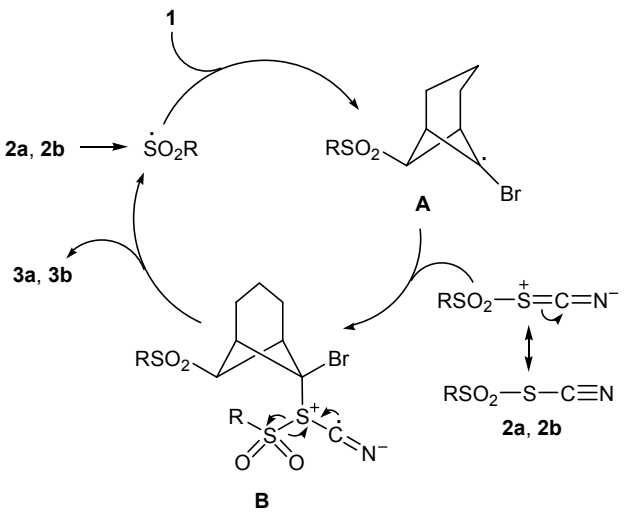


Structure of the molecule of 7-*syn*-benzenesulfonyl-6-*endo*-bromo-6-*exo*-thiocyanatobicyclo[3.1.1]heptane (**3a**) according to the X-ray diffraction data.

the benzene ring and thiocyanato group with respect to the $C^3C^6C^7$ plane at the same side of the latter. Like 6,7-di- and 6,6,7-trisubstituted norpinanes with a planar trimethylene bridge studied previously [5–8], compound **3a** showed a broadened singlet due to 1-H and 5-H in the ^{1}H NMR spectrum.

Thus, the reaction of bromotricycloheptane **1** with sulfonyl thiocyanates is analogous to previously reported sulfohalogenation [9, 10] and sulfonation [11] of the same substrate, i.e., it involves exclusively the C^1–C^7 bond with complete regio- and stereoselectivity, yielding norpinane adducts **3a** and **3b**. Taking into account that no isothiocyanato derivatives were formed in the addition of arene(alkane)sulfonyl thiocyanates to both tricycloheptanes [1, 2] and unsaturated compounds [2, 12–14], we presumed that chain transfer in these reactions occurs as radical substitution at the thiocyanate sulfur atom, i.e., without participation of discrete NCS$^{\cdot}$ species. A probable mechanism of radical addition of sulfonyl thiocyanates to bromotricycloheptane **1** is shown in Scheme 2.

Scheme 2.



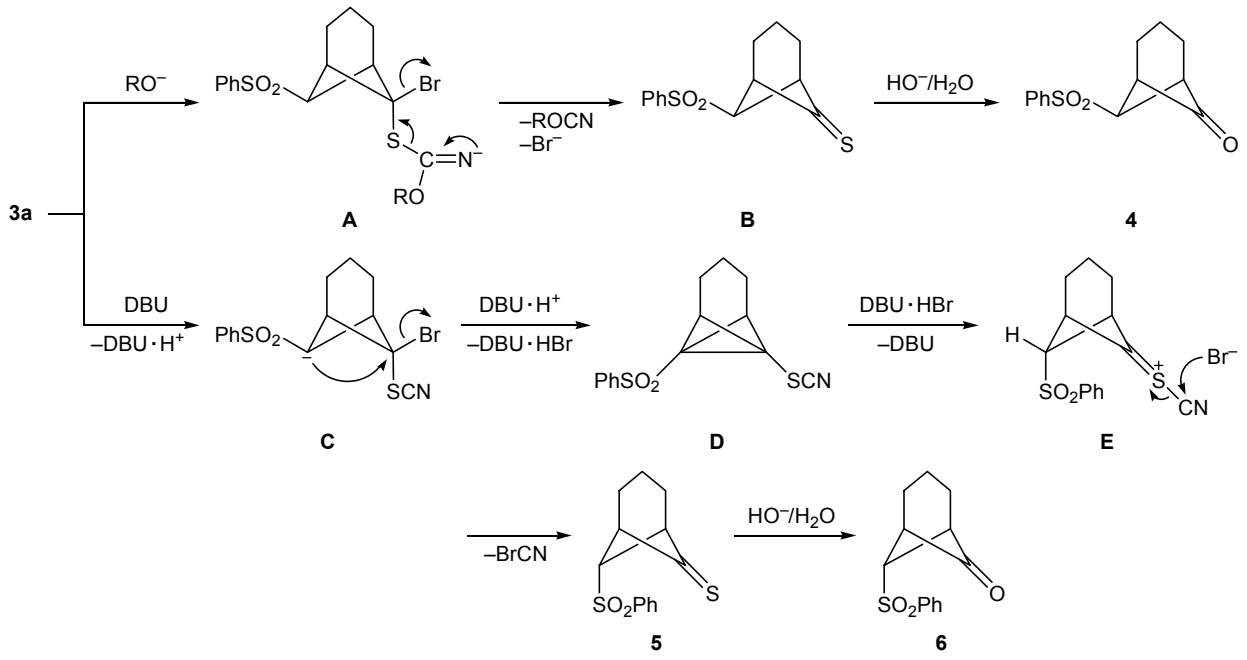
The process is initiated by sulfonyl radical $RSO_2^{\cdot}$ which can be generated from sulfonyl thiocyanate **2** by the action of, e.g., atmospheric oxygen. The attack by $RSO_2^{\cdot}$ on molecule **1** is strictly regio- and stereoselective (cf. other reactions of tricycloheptane hydrocarbons, e.g., of 1-methyltricyclo[4.1.0.0^{2,7}]heptane with sulfonyl compounds RSO_2X [9]), and norpinanyl radical **A** thus formed adds to the sulfur atom of thiocyanate **2**, yielding carbon-centered radical **B**. The latter is converted into final product **3** via elimination of $RSO_2^{\cdot}$ radical which then acts as chain transfer agent. We believe that the thiocyanation of radical **A** with sulfonyl thiocyanate is analogous to the alkenylation of hydrocarbyl radicals with vinyl sulfones [15].

The proposed mechanism accounts for other reactions of tricycloheptane compounds with sulfonyl derivatives RSO_2X, studied by us previously, namely the reactions with *p*-toluenesulfonyl cyanide [1], benzenesulfonyl azide [16], 2-(*p*-tosyl)-1-phenyldiazene [17], allyl sulfones [18], and phenylethynyl sulfones [19]. In the future, we plan to explore these reactions in more detail.

Spatial orientation of the bromine atom in norpinanes **3a** and **3b** is favorable for base-catalyzed 1,3-elimination of hydrogen bromide, which could restore the tricyclo[4.1.0.0^{2,7}]heptane system [8–10]. In order to check the possibility of such transformation we tried different bases (nucleophiles). Treatment of **3a** with potassium *tert*-butoxide in THF at 20°C gave 57% of previously described [20] norpinan-6-one (**4**) as the only product. The same compound was also formed in 35% yield when sulfone **3a** was heated for 20 min in a boiling solution of sodium hydroxide in aqueous dioxane (1 : 1). The reaction of **3a** with 2 equiv of 1,8-diazabicylo[5.4.0]undec-7-ene (DBU) in methylene chloride at 25°C (48 h) afforded 51% of norpinane-6-thione (**5**) whose hydrolysis on heating with sodium hydroxide in aqueous dioxane gave ketone **6** diastereoisomeric to **4** (Scheme 3).

Compounds **4**–**6** were isolated in the pure state. The thioxo group in **5** showed a signal at δ_C 261.6 ppm in the ^{13}C NMR spectrum and a characteristic IR absorption band at 1088 cm^{-1} [3]. The carbonyl carbon signal

Scheme 3.



R = *t*-Bu, H.

of **4** and **6** was located at δ_C ~200 ppm in the ^{13}C NMR spectra, and the carbonyl stretching band was observed at ~1800 cm^{-1} in the IR spectra. The *anti* orientation of the sulfonyl group in molecules **5** and **6** followed from the presence of a singlet signal from the 7-*syn*-H proton in the ^1H NMR spectrum [4].

Presumably, hard nucleophiles such as potassium *tert*-butoxide and sodium hydroxide add to the SCN carbon atom of **3a** with formation of intermediate **A** which loses bromide ion and *tert*-butyl cyanate (or cyanic acid) molecule, yielding thioketone **B**. The latter undergoes fast hydrolysis by the action of sodium hydroxide (or potassium hydroxide formed from *t*-BuOK on exposure to atmospheric moisture during workup) to give ketone **4** as final product.

The reaction takes a different path when compound **3a** is subjected to the action of strongly basic but weakly nucleophilic DBU. Here, the first step is deprotonation of **3a** at the α-position with respect to the sulfonyl group with formation of carbanion **C**. Next follows intramolecular nucleophilic substitution of bromine to give tricycloheptane structure **D** which takes up hydrogen bromide at the C^1–C^7 bond. Some amount of hydrogen bromide is present in the reaction mixture both in a free state and reversibly bound to DBU. The addition of HBr begins with regio- and stereoselective protonation [21, 22] of the bridgehead carbon atom bearing the benzenesulfonyl group, which determines *exo* orientation of the latter in both intermediate bromide **E** and thione **5** formed therefrom via elimination of cyanogen bromide molecule (or its constituents).

It was surprising that, unlike 6-phenyl-6-thiocyanato-substituted analogs [2], norpinane **3a** turned out to be stable toward silver nitrate in aqueous dioxane both at room temperature (24 h) and under reflux conditions (2 h). These findings indirectly indicated that compound **3a** failed to react according to S_N1 mechanism not only by the action of silver ions but also in the presence of bases.

In contrast to norpinane **3a**, treatment of its methanesulfonyl-substituted analog **3b** with potassium *tert*-butoxide, DBU, and other bases under the given conditions resulted in the formation of complex mixtures of unidentified products.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded from solutions in $CDCl_3$ on a Jeol JNM-ECX400 spectrometer at 400 and 100 MHz, respectively, using the residual proton (δ 7.26 ppm) and carbon (δ_C 77.16 ppm) signals of the solvent as reference. The IR spectra were measured in KBr on an InfraLYuM FT-02 spectrometer with Fourier transform. The elemental analyses were

obtained on a VarioMICRO CHNS analyzer. Analytical TLC was performed on Sorbfil plates using light petroleum ether–ethyl acetate (3 : 1) as eluent; the chromatograms were developed in an iodine chamber or under UV light. Initial bromotricycloheptane **1** with a purity of >97% was synthesized according to the procedure described in [23].

Reaction of tricycloheptane 1 with benzene- and methansulfonyl thiocyanates (*general procedure*). Tricycloheptane **1**, 1.73 g (10 mmol) was added to a solution of 10 mmol of benzene- or methanesulfonyl thiocyanate **2a** or **2b** (prepared by reaction of the corresponding sodium sulfinate with thiocyanogen [2]) in 10 mL of anhydrous benzene. The mixture was kept in a tightly capped flask for 7–8 h at 20°C, the progress of the reaction being monitored by TLC. The solvent was removed under reduced pressure (water-jet pump), and the solid residue was analyzed by ^{1}H NMR and purified by crystallization. Compound **3a** or **3b** was isolated as the only product.

7-*syn*-Benzenesulfonyl-6-*endo*-bromo-6-*exo*-thiocyanatobicyclo[3.1.1]heptane (3a). Yield 58%, colorless crystals, mp 175–176°C. IR spectrum, ν, cm^{-1}: 2156 w, 1446 m, 1331 m, 1304 m (SO_2, asym.), 1153 v.s (SO_2, sym.), 1092 m, 721 m, 687 m, 617 s. ^{1}H NMR spectrum, δ, ppm: 1.78–1.89 m (1H, 3-*endo*-H), 2.09–2.19 m (1H, 3-*exo*-H), 2.22–2.28 m (2H, 2-*endo*-H, 4-*endo*-H), 2.69–2.76 m (2H, 2-*exo*-H, 4-*exo*-H), 3.10 br.s (2H, 1-H, 5-H), 4.08 t (1H, 7-*anti*-H, J = 5.4 Hz), 7.62 t (2H, H_{arom}, J = 7.7 Hz), 7.70 t (1H, H_{arom}, J = 7.3 Hz), 7.91 d (2H, H_{arom}, J = 7.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.6 (C^3), 25.4 (C^2, C^4), 52.3 (C^1, C^5), 59.4 (C^7), 70.2 (C^6), 109.0 (SCN), 127.6 (2C, C_{arom}), 129.9 (2C, C_{arom}), 134.4 (C_{arom}), 140.0 w (C_{arom}). Found, %: C 45.31; H 3.89; N 3.69; S 17.14. $C_{14}H_{14}BrNO_2S_2$. Calculated, %: C 45.17; H 3.79; N 3.76; S 17.22.

6-*endo*-Bromo-7-*syn*-methanesulfonyl-6-*exo*-thiocyanatobicyclo[3.1.1]heptane (3b). Yield 48%, colorless crystals, mp 178–179°C (from hexane–$CHCl_3$). IR spectrum, ν, cm^{-1}: 2164 m, 1342 s, 1304 s (SO_2, asym.), 1257 m, 1138 v.s (SO_2, sym.), 1003 m, 968 m, 753 m, 563 m. ^{1}H NMR spectrum, δ, ppm: 1.72–1.87 m (1H, 3-*endo*-H), 1.92–2.07 m (1H, 3-*exo*-H), 2.16–2.28 m (2H, 2-*endo*-H, 4-*endo*-H), 2.53–2.66 m (2H, 2-*exo*-H, 4-*exo*-H), 2.97 s (3H, CH_3), 3.24 br.d (2H, 1-H, 5-H, J = 5.6 Hz), 4.12 t (1H, 7-*anti*-H, J = 5.6 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.2 (C^3), 24.9 (C^2, C^4), 42.7 (CH_3), 52.0 (C^1, C^5), 57.2 (C^7), 69.9 (C^6), 108.8 (SCN). Found, %: C 34.71; H 3.99; N 4.66; S 20.40. $C_9H_{12}BrNO_2S_2$. Calculated, %: C 34.85; H 3.90; N 4.52; S 20.67.

X-Ray analysis of compound 3a. The X-ray diffraction data for compound **3a** were obtained from a 0.19×0.15×0.04-mm transparent prismatic single crystal at 293(2) K on an Oxford Diffraction Xcalibur Gemini S automated four-circle diffractometer (MoK_α radiation, graphite monochromator, Sapphire III CCD detector, ω-scanning, $2\theta_{max}$ 52.74°; $-21 \le h \le 21$, $-7 \le k \le 7$, $-16 \le l \le 16$). Total of 19085 reflection intensities were measured; averaging of equivalent reflections left 3016 independent reflections (R_{int} = 0.0166), including 2615 reflections with $I > 2\sigma(I)$. The unit cell parameters were determined using CrysAlisPro [24]. A correction for absorption was applied empirically by SCALE3 ABSPACK algorithm [25]. Monoclinic crystal system, space group $P2_1/c$; unit cell parameters: a = 17.593(3), b = 6.2817(10), c = 13.422(2) Å; β = 94.268(14); V = 1479.3(4) Å^3; Z = 4; M 372.29; d_{calc} = 1.672 g/cm^3; μ = 3.061 mm^{-1}; F(000) = 752. The structure was solved by the direct method and was refined against F^2 by the full-matrix least-squares procedure in anisotropic approximation for non-hydrogen atoms using SHELX-97 [26] and WinGX [27]. Number of independent variables 182, goodness of fit 1.058; residual electron density dispersion –0.603 and 0.541 $\bar{e}$ Å^{-3}; final divergence factors: R_1 = 0.0358 [for reflections with $I > 2\sigma(I)$], wR_2 = 0.0893 (for all independent reflections). The positions of hydrogen atoms were calculated geometrically and were refined according to the riding model [U(H) = $1.2U_{eq}$(C)]; weight scheme $w = 1/[\sigma^2(F_o^2) + (0.0431P)^2 + 0.8380P]$, where $P = (F_o^2 + 2F_c^2)/3$. The molecular structure of **3a** was plotted using ORTEP-3 [28]. The X-ray diffractin data for compound **3a** were deposited to the Cambridge Crystallographic Data Centre (entry no. CCDC 1051139).

7-*endo*-(Benzenesulfonyl)bicyclo[3.1.1]heptan-6-one (4). Powdered potassium *tert*-butoxide, 123 mg (1.1 mmol), was added under argon to a solution of 372 mg (1 mmol) of norpinane **3a** in 20 mL of anhydrous THF. The mixture was stirred for 1 h at 20°C, diluted with 30 mL of water, and extracted with diethyl ether (3×15 mL). The combined extracts were washed with brine and water and dried over $MgSO_4$, the solvent was removed, and the residue was purified by recrystallization. Yield 153 mg (51%), mp 133–134°C. The ^{1}H and ^{13}C NMR spectra of the product were identical to those given in [19]. IR spectrum, ν, cm^{-1}: 1802 s (C=O), 1447 m, 1319 m (SO_2, asym.), 1289 s,

1150 v.s (SO_2, sym.), 1088 m, 764 m, 725 s, 691 m, 606 s, 559 m.

7-*exo*-(Benzenesulfonyl)bicyclo[3.1.1]heptane-6-thione (5). 1,8-Diazabicylo[5.4.0]undec-7-ene, 300 mg (2 mmol), was added dropwise to a solution of 340 mg (0.9 mmol) of compound **3a** in 5 mL of anhydrous methylene chloride. The mixture was stirred for 48 h at 25°C, the solvent was removed, and the residue was purified by dry-column flash chromatography (ethyl acetate–hexane, 1:3). Yield 123 mg (51%), light orange crystals, mp 142–143°C (from hexane–*t*-BuOMe). IR spectrum, ν, cm^{-1}: 1446 m, 1362 m, 1303 s (SO_2, asym.), 1273 m, 1242 m, 1165 m, 1146 v.s (SO_2, sym.), 1088 m (C=C), 752 m, 721 m, 687 m, 594 m, 586 m, 548 m. ^{1}H NMR spectrum, δ, ppm: 1.58–1.80 m (2H, 3-H), 2.89–2.55 m (4H, 2-H, 4-H), 3.52 s (2H, 1-H, 5-H), 3.75 s (1H, 7-*endo*-H), 7.55 t (2H, H_{arom}, J = 7.8 Hz), 7.58 t (1H, H_{arom}, J = 7.3 Hz), 7.90 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum, δ_C, ppm: 15.5 (C^3), 38.8 (C^2, C^4), 63.5 (C^7), 64.1 (C^1, C^5), 129.0 (2C, C_{arom}), 129.6 (2C, C_{arom}), 134.5 (C_{arom}), 137.6 w (C_{arom}), 261.6 (C=S). Found, %: C 52.71; H 5.49; S 24.24. $C_{13}H_{14}O_2S_2$. Calculated, %: C 58.62; H 5.30; S 24.07.

7-*exo*-(Benzenesulfonyl)bicyclo[3.1.1]heptan-6-one (6). Thioketone **5**, 100 mg (0.38 mmol), was dissolved in 5 mL of dioxane, 5 mL of 5 M aqueous sodium hydroxide and 90 mg of benzyl(triethyl)ammonium chloride were added, and the mixture was stirred for 3 h at 50°C. The mixture was then cooled to 0°C, neutralized with 4 mL of dilute (1:1) aqueous HCl, and extracted with CH_2Cl_2 (3×15 mL). The combined extracts were dried over $MgSO_4$ and evaporated under reduced pressure, and the residue was subjected to dry-column flash chromatography (ethyl acetate–hexane, 1:2). Yield 55 mg (58%), colorless crystals, mp 128–129°C (from hexane–$CHCl_3$). IR spectrum, ν, cm^{-1}: 2970 w, 2947 w, 1797 v.s. (C=O), 1450 w, 1308 s (SO_2, asym.), 1265 w, 1146 v.s (SO_2, sym.), 1090 m, 1030 w, 918 w, 756 w, 717 w, 694 m, 594 m, 552 m. ^{1}H NMR spectrum, δ, ppm: 1.58–1.74 m (2H, 3-H), 2.33–2.47 m (4H, 2-H, 4-H), 3.40 br.s (2H, 1-H, 5-H), 3.36 s (1H, 7-*endo*-H), 7.60 t.t (2H, H_{arom}, J = 1.3, 7.3 Hz), 7.77 t.t (1H, H_{arom}, J = 1.7, 7.3 Hz), 7.93 d.t (2H, H_{arom}, J = 1.7, 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 16.1 (C^3), 34.3 (C^2, C^4), 58.8 (C^1, C^5), 61.3 (C^7), 128.7 (2C, C_{arom}), 129.7 (2C, C_{arom}), 134.4 (C_{arom}), 137.5 (C_{arom}), 207.0 (C=O). Found, %: C 62.42; H 5.69; S 12.77. $C_{13}H_{14}O_3S$. Calculated, %: C 62.38; H 5.64; S 12.81.

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