Synthesis and Spectral Properties of 2,3-Dihydro-4-(*para*-substituted-phenyl)-7-[(*o*-, *m*-, and *p*-substituted)phenoxy]-1*H*-1,5-benzodiazepine-2-thiones

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A series of twelve new 2,3-dihydro-4-(*para*-substituted-phenyl)-7-[(*o*-, *m*-, and *p*-substituted)phenoxy]-1*H*-1,5-benzodiazepine-2-thiones, which have potentially useful pharmacological properties, has been synthesized by condensing the 3,3-dimercapto-1-(*para*-substituted phenyl)-2-propen-1-one with 3,4-diaminophenyl-*R*-phenyl ethers. The structure of all products was corroborated by ir, ^{1}H-nmr, ^{13}C-nmr and ms.

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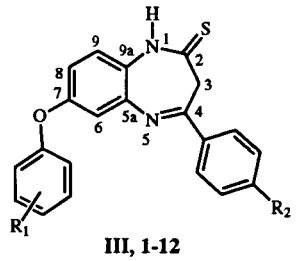
In the course of synthesis and spectral properties studies of compounds with possible pharmacological activity, we have previously reported the synthesis of 1*H*-1,5-benzodiazepine-2-thiones [3], which are close analogues of 1,5-benzodiazepin-2-ones, known to have anticonvulsant activity. The study also demonstrated that these derivatives were more potent that clobazam and desmethyl clobazam [4].

Continuing with the program directed towards the synthesis and spectral property determination of 1*H*-1,5-benzodiazepine-2-thiones derivatives with possible pharmacological activity, we describe in this report the synthesis of twelve new compounds 2,3-dihydro-4-(*para*-substituted-phenyl)-7-[(*o*-, *m*-, and *p*-substituted) phenoxy]-1*H*-1,5-benzodiazepine-2-thiones **III, 1-12** (Scheme 1) as shown in Scheme 2.

Scheme 1

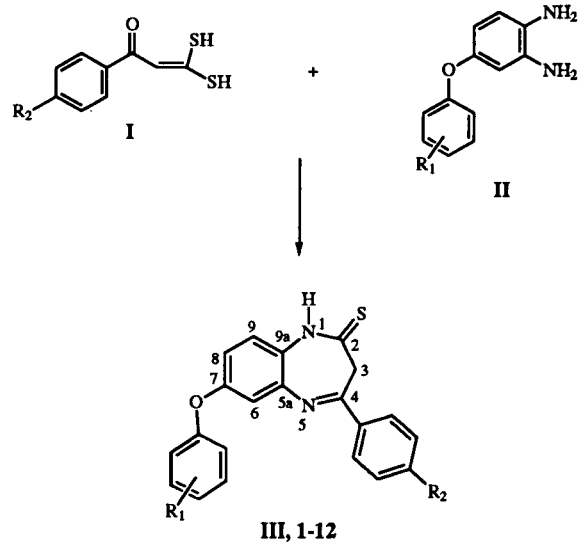


III, 1-12

	R_1	R_2
1	H	Cl
2	H	Br
3	H	OCH_3
4	*o*-CH_3	Cl
5	*o*-CH_3	Br
6	*o*-CH_3	OCH_3
7	*m*-CH_3	Cl
8	*m*-CH_3	Br
9	*m*-CH_3	OCH_3
10	*p*-CH_3	Cl
11	*p*-CH_3	Br
12	*p*-CH_3	OCH_3

The reaction of Compound **I** with **II**, has been performed in anhydrous *ortho*-xylene heated at 130-135° for five hours.

Scheme 2



III, 1-12

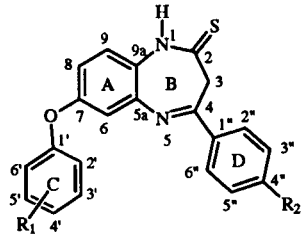
The 1*H*-1,5-benzodiazepine-2-thiones **III, 1-12** have been obtained in 18-40% yield.

The infrared spectrum of compounds **1-12** displayed absorptions at 3199-3130 cm^{-1} for N-H stretching; at 1594-1584 cm^{-1} for C=N stretching; at 1240-1234 and 1184-1180 cm^{-1} for C-N stretching; at 1265-1257 and 1105-1013 cm^{-1} for C-O stretching and the corresponding absorptions for aromatic and R-substituents.

In the ^{1}H nmr spectra the presence of three proton signals at δ 2.18-2.32 singlet were assigned to the methyl protons joined at C-2', C-3' and C-4' of the phenyl "C" ring; the presence of two proton signals at δ 3.83-3.92 broad was consistent with the methylene protons of the C-3. The presence of three proton signals at δ 6.27-7.38 multiplet was assigned to the aromatic protons of C-6, C-8 and C-9 of the benzodiazepine framework. The other aromatic protons appeared as a multiplet and AA'BB' system at δ 6.88-8.17, the presence of one proton signal at δ 12.35-12.55 broad with deuterium oxide exchangeable

Table 1

^{13}C NMR Spectral Data for Compounds **1-12**



III, 1-12

Compounds	1	2	3	4	5	6	7	8	9	10	11	12
R1	H	H	H	*o*-CH_3	*o*-CH_3	*o*-CH_3	*m*-CH_3	*m*-CH_3	*m*-CH_3	*p*-CH_3	*p*-CH_3	*p*-CH_3
R2	Cl	Br	OCH_3	Cl	Br	OCH_3	Cl	Br	OCH_3	Cl	Br	OCH_3
C-2	190.0	191.5	191.7	191.5	191.3	191.5	191.5	190.0	191.7	191.4	190.0	192.0
C-3	47.7	47.6	47.4	47.7	47.5	47.4	47.6	47.5	47.4	47.7	47.6	47.5
C-4	158.3	158.3	158.7	157.3	158.3	158.6	158.7	158.3	158.6	158.3	158.3	157.0
C-5a	141.6	141.5	142.1	141.6	141.5	141.9	141.5	141.5	141.9	141.6	141.4	141.1
C-6	115.6	115.6	115.6	115.5	113.7	114.1	115.5	115.5	114.9	114.9	114.9	114.1
C-7	155.6	155.9	156.1	154.4	154.7	154.6	154.2	154.6	155.9	154.8	154.7	154.4
C-8	116.9	116.7	116.3	116.9	115.6	114.9	116.7	116.0	115.9	116.5	116.4	115.8
C-9	123.8	123.2	123.7	123.8	123.6	123.7	123.6	123.6	123.5	123.8	123.6	123.7
C-9a	127.2	127.1	127.2	127.1	125.1	127.3	127.0	125.1	127.0	128.5	126.8	129.8
C-1'	154.2	154.1	154.1	155.9	153.2	153.3	155.8	154.3	154.1	153.4	153.4	153.3
C-2'	119.2	118.9	119.0	116.2	126.5	126.5	116.0	116.7	116.1	119.4	119.2	119.4
C-3'	130.1	129.8	130.1	136.6	131.2	131.4	136.2	139.7	139.7	130.5	129.6	129.9
C-4'	124.0	123.7	123.9	124.7	124.5	124.4	124.5	124.5	124.4	126.9	125.1	129.2
C-5'	130.1	129.8	130.1	129.8	129.5	130.3	129.6	127.0	129.5	130.5	129.6	129.9
C-6'	119.2	118.9	119.0	119.7	119.9	119.8	119.5	119.5	119.4	119.4	119.2	119.4
C-1"	135.1	135.3	128.6	135.0	135.3	128.6	135.0	135.3	128.6	133.3	133.1	128.7
C-2";C-6"	128.7	128.5	129.9	129.6	128.9	129.7	129.4	129.6	129.7	128.7	130.3	130.5
C-3";C-5"	129.6	131.4	113.9	128.6	131.7	113.8	128.5	131.5	113.8	129.6	131.4	114.0
C-4"	136.4	135.3	161.9	141.6	135.3	161.8	139.7	135.3	161.0	136.3	135.3	161.7
R1	–	–	–	20.8	15.4	15.4	20.6	20.6	20.6	20.2	20.0	20.2
R2	–	–	55.4	–	–	55.3	–	–	55.3	–	–	55.5

Note: The numbering of the phenyl rings is only for the assignment of the chemical shifts of the carbons in ^{13}C nmr spectra

was consistent with the proton of the N-H; the presence of three proton signals at δ 3.83-3.86 singlet were assigned to the methoxy protons for the R_2-substituent.

The ^{13}C nmr spectra of compounds **1-12** are given in Table 1, and the signals were confirmed by using HETCOR, Long Range HETCOR, COSY AND NOESY nmr experiments operating at 500 MHz.

The mass spectra of the compounds **1-12** include ions at m/z $[M-15]^+$, $[M-32]^+$, $[M-33]^+$, $[M-34]^+$, $[M-58]^+$, $[M-R_2]^+$, $[M-(33+R_2)]^+$, $[249+R_2]^+$, $[208+R_2]^+$, $[193+R_2]^+$, $[120+R_2]^+$, $[76+R_2]^+$ and $[76+R_1]^+$. The molecular ion is the base peak, and the main fragmentation was consistent with the assigned structures. The proposed fragmentation pathways leading to the formation of a number of important daughter ions have been confirmed of the corresponding parent ion spectra by collision-induced dissociation (CID) experiments. The elemental composition of the molecular ion and the principal fragment ions was determined by exact mass measurements.

EXPERIMENTAL

The ir spectra were recorded on a Nicolet Magna TR-750 spectrophotometer. The ^1H-nmr spectra were recorded on a Varian Unity-300 Spectrometer operating at 300 MHz and the ^{13}C-nmr spectra were recorded on a Varian Unity Plus-500 spectrometer operating at 500 MHz, in deuteriodimethyl sulfoxide solution containing tetramethyl silane as the internal standard with chemical shifts δ (ppm) expressed downfield from tetramethylsilane. The mass spectra were measured on a JEOL JMS-AX505 and JEOL MS-SX 102A High Resolution Mass Spectrometer with accurate mass determination of the molecular ion, using the direct inlet system. The spectra were recorded by electron impact at an ionization chamber temperature of 190° and ionizing electron energy of 70 eV.

General Procedure for the Synthesis of the 2,3-Dihydro-4-(*para*-substituted-phenyl)-7-[(*o*-, *m*-, and *p*-substituted)phenoxy]-1*H*-1,5-benzodiazepine-2-thiones, **III, 1-12**.

A mixture of 0.024 mole of 3,3-dimecapto-1-[(*p*-substituted)phenyl]-2-propen-1-one, **I**, 0.024 mole of 3,4-diaminophenyl-R_1-phenyl ether, **II**, in 150 ml of dry *ortho*-

xylene was heated at 130-135° for five hours. After cooling, the crystals were collected and washed with hexane-acetone to yield the compounds **III**, **1-12** (18-40%).

2,3-Dihydro-4-(*para*-chlorophenyl)-7-phenoxy-1*H*-1,5-benzodiazepine-2-thione (**1**).

This compound was obtained as yellowish needles in 19% yield, mp 228°; ir (nujol mull): ν N-H 3157, C=N 1590, C-N 1234 and 1175, C-O 1262 and 1103 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 3.90 (bs, 2H, 3-H), 6.91 (d, 1H, J = 2.7 Hz, 6-H), 7.03 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 7.10 and 7.38 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring, 2'-H, 3'-H, 5'-H, 6'-H), 7.19 (d, d, t, 1H, J = 0.8, 3.0, 7.5 Hz, 4'-H), 7.44 (d, 1H, J = 8.1 Hz, 9-H), 7.59 and 8.17 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 12.46 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 378 (M^+), m/z 380 $[M+2]^+$, m/z 382 $[M+4]^+$.

Anal. Calcd. for $C_{21}H_{15}ClN_2OS$: C, 66.57; H, 3.99; N, 7.40. Found: C, 66.45; H, 4.07; N, 7.47.

2,3-Dihydro-4-(*para*-bromophenyl)-7-phenoxy-1*H*-1,5-benzodiazepine-2-thione (**2**).

This compound was obtained as yellowish needles in 18% yield, mp 230°; ir (nujol mull): ν N-H 3159, C=N 1586, C-N 1237 and 1170, C-O 1265 and 1076 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 3.92 (bs, 2H, 3-H), 6.92 (d, 1H, J = 3.3 Hz, 6-H), 7.02 (d, d, 1H, J = 3.0, 8.4 Hz, 8-H), 7.08 and 7.41 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring, 2'-H, 3'-H, 5'-H, 6'-H), 7.19 (d, d, t, 1H, J = 0.8, 3.0, 7.6 Hz, 4'-H), 7.39 (d, 1H, J = 8.7 Hz, 9-H), 7.72 and 8.09 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 12.44 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 422 (M^+), m/z 424 $[M+2]^+$, m/z 426 $[M+4]^+$.

Anal. Calcd. for $C_{21}H_{15}BrN_2OS$: C, 59.58; H, 3.57; N, 6.62. Found: C, 59.65; H, 3.63; N, 6.57.

2,3-Dihydro-4-(*para*-methoxyphenyl)-7-phenoxy-1*H*-1,5-benzodiazepine-2-thione (**3**).

This compound was obtained as yellowish needles in 21% yield, mp 215°; ir (nujol mull): ν N-H 3130, C=N 1592, C-N 1240 and 1103, C-O 1267 and 1033 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 3.82 (s, 3H, CH_3-O), 3.85 (bs, 2H, 3-H), 6.72 (d, 1H, J = 3.0 Hz, 6-H), 6.98 (d, d, 1H, J = 3.0, 8.7 Hz, 8-H), 7.06 and 8.13 (AA'BB', 4H, J = 9.0 Hz, phenyl protons of "D" ring), 7.09 and 7.43 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring, 2'-H, 3'-H, 5'-H, 6'-H), 7.18 (d, d, t, 1H, J = 0.7, 2.8, 7.5 Hz, 4'-H), 7.37 (d, 1H, J = 8.4 Hz, 9-H), 12.48 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 374 (M^+), m/z 376 $[M+2]^+$.

Anal. Calcd. for$C_{22}H_{18}N_2O_2S$: C, 70.56; H, 4.85; N, 7.48. Found: C, 70.50; H, 4.75; N, 7.56.

2,3-Dihydro-4-(*para*-chlorophenyl)-7-(*o*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**4**).

This compound was obtained as yellowish needles in 21% yield, mp 218°; ir (nujol mull): ν N-H 3146, C=N 1584, C-N 1234 and 1166, C-O 1261 and 1098 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.30 (s, 3H, CH_3-$C_{2'}$), 3.91 (bs, 2H, 3-H), 6.88 (d, 1H, J = 3.0 Hz, 6-H), 6.91 (d, d, 1H, J = 2.1, 7.4 Hz, 6'-H), 7.0 (d, t, 1H, J = 1.3, 7.5 Hz, 4'-H), 7.03 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 7.29 (d, t, 1H, J = 1.2, 7.5 Hz, 5'-H), 7.30 (d, d, 1H, J = 1.2, 8.4 Hz, 3'-H), 7.36 (d, 1H, J = 8.7 Hz, 9-H), 7.58 and 8.17 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 12.55 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 392 (M^+), m/z 394 $[M+2]^+$, m/z 396 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}ClN_2OS$: C, 67.25; H, 4.36; N, 7.13. Found: C, 67.35; H, 4.28; N, 7.19.

2,3-Dihydro-4-(*para*-bromophenyl)-7-(*o*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**5**).

This compound was obtained as brownish needles in 19% yield, mp 213°; ir (nujol mull): ν N-H 3199, C=N 1587, C-N 1238 and 1184, C-O 1242 and 1075 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.19 (s, 3H, CH_3-$C_{2'}$), 3.90 (bs, 2H, 3-H), 6.74 (d, 1H, J = 2.7 Hz, 6-H), 6.95 (d, d, 1H, J = 3.0, 9.0 Hz, 8-H), 7.01 (d, d, 1H, J = 2.1, 7.4 Hz, 6'-H), 7.16 (d, t, 1H, J = 1.3, 7.8 Hz, 4'-H), 7.23 (d, t, 1H, J = 1.8, 7.8 Hz, 5'-H), 7.25 (d, d, 1H, J = 1.8, 7.4 Hz, 3'-H), 7.36 (d, 1H, J = 8.7 Hz, 9-H), 7.71 and 8.09 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 12.42 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 436 (M^+), m/z 438 $[M+2]^+$, m/z 440 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}BrN_2OS$: C, 60.42; H, 3.92; N, 6.41. Found: C, 60.49; H, 3.99; N, 6.33.

2,3-Dihydro-4-(*para*-methoxyphenyl)-7-(*o*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**6**).

This compound was obtained as orange needles in 24% yield, mp 210°; ir (nujol mull): ν N-H 3167, C=N 1594, C-N 1235 and 1178, C-O 1257 and 1104 cm^{-1}; ^{1}H-nmr (deuterio dimethyl sulfoxide): δ 2.22 (s, 3H, CH_3-$C_{2'}$), 3.83 (bs, 2H, 3-H), 3.86 (s, 3H, CH_3-O), 6.72 (d, 1H, J = 2.7 Hz, 6-H), 6.90 (d, d, 1H, J = 3.0, 9.0 Hz, 8-H), 7.00 (d, d, 1H, J = 1.8, 8.0 Hz, 6'-H), 7.05 and 8.16 (AA'BB', 4H, J = 9.0 Hz, phenyl protons of "D" ring), 7.14 (d, t, 1H, J = 1.8, 7.5 Hz, 4'-H), 7.24 (d, t, 1H, J = 1.8, 7.5 Hz, 5'-H), 7.26 (d, d, 1H, J = 2.1, 7.5 Hz, 3'-H), 7.35 (d, 1H, J = 9.0 Hz, 9-H), 12.35 (bs, 1H, N-H, deuterium oxide exchangeable): ms: m/z 388 (M^+), m/z 390 $[M+2]^+$.

Anal. Calcd. for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 71.23; H, 5.09; N, 7.28.

2,3-Dihydro-4-(*para*-chlorophenyl)-7-(*m*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**7**).

This compound was obtained as yellowish needles in 28% yield, mp 218°; ir (nujol mull): ν N-H 3140, C=N 1587, C-N 1235 and 1164, C-O 1262 and 1013 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.30 (s, 3H, CH_3-$C_{3'}$), 3.92 (bs, 2H, 3-H), 6.86 (d, 1H, J = 2.4 Hz, 6-H), 6.90 (d, d, d, 1H, J = 0.6, 2.4, 7.6 Hz, 6'-H), 6.93 (d, d, 1H, J = 2.3, 8.7 Hz, 2'-H), 7.00 (d, d, 1H, J = 2.7, 8.5 Hz, 8-H), 7.24 (d, d, d, 1H, J = 0.6, 2.2, 7.8 Hz, 4'-H), 7.30 (d, t, 1H, J = 1.2, 7.9 Hz, 5'-H), 7.38 (d, 1H, J = 9.0 Hz, 9-H), 7.58 and 8.17 (AA'BB', 4H, J = 9.0 Hz, phenyl protons of "D" ring), 12.45 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 392 (M^+), m/z 394 $[M+2]^+$, m/z 396 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}ClN_2OS$: C, 67.25; H, 4.36; N, 7.13. Found: C, 67.18; H, 4.42; N, 7.06.

2,3-Dihydro-4-(*para*-bromophenyl)-7-(*m*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**8**).

This compound was obtained as yellowish needles in 26% yield, mp 214°; ir (nujol mull): ν N-H 3163, C=N 1582, C-N 1233 and 1102, C-O 1260 and 1055 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.32 (s, 3H, CH_3-$C_{3'}$), 3.92 (bs, 2H, 3-H), 6.86 (d, 1H, J = 3.0 Hz, 6-H), 6.91 (d, d, 1H, J = 2.3, 7.5 Hz, 2'-H), 6.92 (d, d, 1H, J = 2.7, 7.8 Hz, 8-H), 6.98 (d, d, d, 1H, J =

0.5, 2.2, 7.5 Hz, 6'-H), 7.00 (d, d, d, 1H, J = 0.5, 2.1, 7.8 Hz, 4'-H), 7.29 (d, t, 1H, J = 1.4, 7.8 Hz, 5'-H), 7.38 (d, 1H, J = 9.0 Hz, 9-H), 7.72 and 8.09 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 12.45 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 436 (M^+), m/z 438 $[M+2]^+$, m/z 440 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}BrN_2OS$: C, 60.42; H, 3.92; N, 6.41. Found: C, 60.47; H, 3.86; N, 6.35.

2,3-Dihydro-4-(*para*-methoxyphenyl)-7-(*m*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**9**).

This compound was obtained as brownish needles in 25% yield, mp 214°; ir (nujol mull): ν N-H 3152, C=N 1592, C-N 1247 and 1103, C-O 1253 and 1027 cm^{-1}, ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.20 (s, 3H, CH_3-$C_{3'}$), 3.83 (s, 3H, CH_3-O), 3.88 (bs, 2H, 3-H), 6.87 (d, 1H, J = 3.0 Hz, 6-H), 6.88 (d, d, d, 1H, J = 0.6, 2.1, 7.4 Hz, 6'-H), 6.91 (d, d, 1H, J = 2.4, 7.8 Hz, 2'-H), 6.93 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 7.02 (d, d, d, 1H, J = 0.6, 2.3, 7.5 Hz, 4'-H), 7.06 and 8.13 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "D" ring), 7.29 (d, t, 1H, J = 1.2, 7.8 Hz, 5'-H), 7.36 (d, 1H, J = 9.0 Hz, 9-H), 12.38 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 388 (M^+), m/z 390 $[M+2]^+$.

Anal. Calcd. for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 71.17; H, 5.29; N, 7.30.

2,3-Dihydro-4-(*para*-chlorophenyl)-7-(*p*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**10**).

This compound was obtained as yellowish needles in 19% yield, mp 232°; ir (nujol mull): ν N-H 3140, C=N 1588, C-N 1237 and 1073, C-O 1261 and 1055 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.28 (s, 3H, CH_3-$C_{4'}$), 3.90 (bs, 2H, 3-H), 6.83 (d, 1H, J = 2.4 Hz, 6-H), 6.98 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 7.00 and 7.23 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring), 7.36 (d, 1H, J = 9.0 Hz, 9-H), 7.59 and 8.16 (AA'BB', 4H, J = 9.0 Hz, phenyl protons of "D" ring), 12.53 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 392 (M^+), m/z 394 $[M+2]^+$, m/z 396 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}ClN_2OS$: C, 67.25; H, 4.36; N, 7.13. Found: C, 67.29; H, 4.46; N, 7.07.

2,3-Dihydro-4-(*para*-bromophenyl)-7-(*p*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**11**).

This compound was obtained as yellowish needles in 24% yield, mp 218°; ir (nujol mull): ν N-H 3145, C=N 1586, C-N 1236 and 1101, C-O 1262 and 1075 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide): δ 2.30 (s, 3H, CH_3-$C_{4'}$), 3.90 (bs, 2H, 3-H), 6.80 (d, 1H, J = 2.7, 6-H), 6.99 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 7.17 and 7.43 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring), 7.36 (d, 1H, J = 8.7 Hz, 9-H), 7.71 and 8.09 (AA'BB', 4H, J = 8.4 Hz, phenyl protons of "D" ring), 12.44 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 436 (M^+), m/z 438 $[M+2]^+$, m/z 440 $[M+4]^+$.

Anal. Calcd. for $C_{22}H_{17}BrN_2OS$: C, 60.42; H, 3.92; N, 6.41. Found: C, 60.53; H, 3.84; N, 6.32.

2,3-Dihydro-4-(*para*-methoxyphenyl)-7-(*p*-methylphenoxy)-1*H*-1,5-benzodiazepine-2-thione (**12**).

This compound was obtained as yellowish needles in 18% yield, mp 211°; ir (nujol mull): ν N-H 3133, C=N 1594, C-N 1240 and 1045, C-O 1259 and 1029 cm^{-1}; ^{1}H-nmr (deuteriodimethyl sulfoxide); δ 2.30 (s, 3H, CH_3-$C_{4'}$), 3.84 (s, 3H, CH_3-O), 3.87 (bs, 2H, 3-H), 6.90 (d, 1H, J = 2.7 Hz, 6-H), 6.94 (d, d, 1H, J = 2.7, 8.7 Hz, 8-H), 6.99 and 7.22 (AA'BB', 4H, J = 8.7 Hz, phenyl protons of "C" ring), 7.05 and 8.07 (AA'BB', 4H, J = 9.0 Hz, phenyl protons of "D" ring), 7.38 (d, 1H, J = 9.0 Hz, 9-H), 12.46 (bs, 1H, N-H, deuterium oxide exchangeable); ms: m/z 388 (M^+), m/z 390 $[M+2]^+$.

Anal. Calcd. for $C_{23}H_{20}N_2O_2S$: C, 71.11; H, 5.19; N, 7.21. Found: C, 71.01; H, 5.08; N, 7.28.

REFERENCES AND NOTES

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