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A new synthesis to obtain eleven novel derivatives of 11-[(*o*-; *m*-; and *p*-substituted)-phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-ones with possible pharmacological activity in the central nervous system in two efficient steps has been developed. The final products were obtained by condensation and cyclization between 3-[4-chloro-1,2-phenylenediamine]-5,5-dimethyl-2-cyclohexenone with (*o*-; *m*-; and *p*-substituted)benzaldehyde. The structure of all products was corroborated by ir, ¹H-nmr, ¹³C-nmr and high resolution in ms.

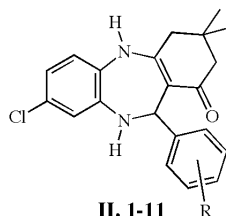
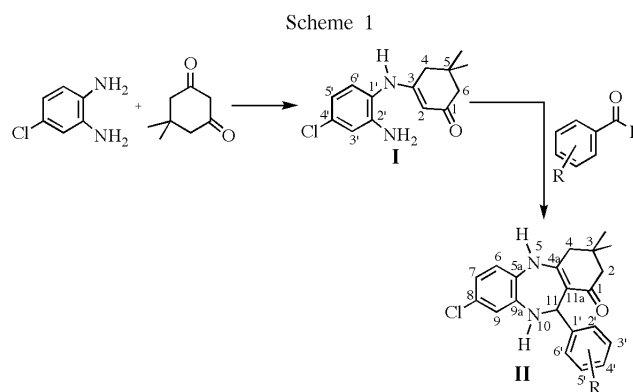
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Clozapine is a piperidine derivative of the benzodiazepine family and it is an atypical antipsychotic agent with proven efficacy in the management of refractory schizophrenia [3-4], and is particularly significant because it lacks extrapyramidal side-effects in humans [5]. Recently, research has been carried out on this compound to confirm its pharmacological activity as an antipsychotic drug [6-10].

We have previously reported the synthesis of the dibenzodiazepine derivatives: dibenzo[*b,e*][1,4]diazepines [11]; 1*H*-dibenzo[*b,e*][1,4]diazepin-1-ones [12] which have potentially useful pharmacological properties.

To continue with the development program directed towards synthesis, spectral properties and determination of useful pharmacological properties of 1,5 and 1,4-benzodiazepine derivatives; we describe in this report the synthesis and spectral properties of eleven new compounds 11-[(*o*-; *m*-; and *p*-substituted)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-

ones **II**, **1-11** (Figure 1), in two efficient steps, as shown in Scheme 1.



II, **1-11**

R

- 1 *o*-Cl
- 2 *m*-Cl
- 3 *p*-Cl
- 4 *o*-OCH₃
- 5 *m*-OCH₃
- 6 *p*-OCH₃
- 7 *o*-Br
- 8 *m*-Br
- 9 *p*-Br
- 10 *m*-NO₂
- 11 *p*-NO₂

Figure 1

Treatment of 4-chloro-1,2-phenylenediamine with 5,5-dimethyl-1,3-cyclohexanedione at reflux in anhydrous benzene with a Dean-Stark apparatus was performed for 26 hours to obtain the 3-[4-chloro-1,2-phenylenediamine]-5,5-dimethyl-2-cyclohexenone **I**, which has been obtained in 60% yields.

A mixture of 1×10^{-3} mole of compound **I**, 1×10^{-3} mole of the corresponding (*o*-; *m*-; and *p*-substituted)benzaldehyde in the presence of 0.5 mL of acetic acid at reflux in 5 mL of ethanol for 1 hour and 45 minutes afforded the 1*H*-dibenzo[*b,e*][1,4]diazepin-1-ones **II**, **1-11** in 61-90% yields.

The infrared spectra of compounds **1-11** displayed absorptions at 3413-1311 cm⁻¹ for N-H stretching, at 1621-1616 cm⁻¹ for C=O stretching, at 1368-1248, and 1394-1235 cm⁻¹ for C-N stretching at 1394-1390 and 1235-1280 cm⁻¹ for C-O stretching and the corresponding absorptions for aromatic and R-substituents.

In the ¹H-nmr spectra the presence of two singlet signals at δ 1.06-1.08 and 1.11-1.14 were assigned to the methyl

protons at C-3. The presence of a doublet at δ 2.01-2.22 and 2.18-2.31 was consistent with the methylene protons at C-2; the presence of other doublet signals at δ 2.38-2.62 and 2.45-3.31 was assigned to the methylene protons on C-4. The presence of a singlet at δ 5.85-6.16 was consistent with the methine proton on C-11. The presence of a broad deuterium oxide exchangeable proton signal at δ 8.22-9.02 was consistent with N-H. The presence of a three-proton multiplet signal at δ 6.27-6.96 was assigned to the aromatic protons at C-6, C-7; and C-9 of the dibenzodiazepine framework. The other aromatic protons, which are members of an AA'BB' system, appeared as a multiplet resonating at δ 6.62-7.96. Signals for the R-substituents are also observed.

The ^{13}C -nmr spectral data for compounds **1-11** are given in Table 1. The signals were confirmed by using HETCOR, COSY, FLOCK, NOESY, and DEPT nmr experiments operating at 300 and 500 MHz. The mass spectra of compounds **1-11** exhibit a stable molecular ion with a relative abundance of 13-47%. The base peak is the ion at m/z

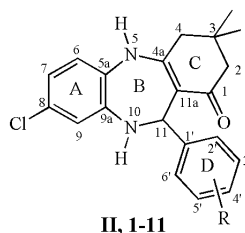
$[\text{M}-(76+\text{R})]^+$. The main fragmentation pathway is consistent with the assigned structures and the mass spectra of the compound **1-11** includes ions of m/z corresponding to molecular ion $[\text{M}]^+$; $[\text{M}-\text{CH}_3]^+$; $[\text{M}-(\text{NH}_2)]^+$; $[\text{M}-\text{R}]^+$; $[\text{M}-(\text{R}+\text{NH}_2)]^+$; $[\text{M}-(77+\text{R})]^+$ (the base peak); $[\text{M}-(\text{C}_4\text{H}_9)]^+$; $[\text{M}-(\text{C}_5\text{H}_8\text{O})]^+$; $[\text{M}-(\text{C}_5\text{H}_9\text{O})]^+$ and m/z 83.

The proposed fragmentation pathways leading to the formation of a number of important daughter ions have been confirmed by the corresponding parent ion spectra, using collision-induced dissociation experiments. The elemental composition of the molecular ion and the principal fragment ion 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 500 spectrometer operat-

Table 1
 ^{13}C NMR Spectral Data for Compounds **1-11**



Compounds R	1 <i>o</i> -Cl	2 <i>m</i> -Cl	3 <i>p</i> -Cl	4 <i>o</i> -OCH ₃	5 <i>m</i> -OCH ₃	6 <i>p</i> -OCH ₃	7 <i>o</i> -Br	8 <i>m</i> -Br	9 <i>p</i> -Br	10 <i>m</i> -NO ₂	11 <i>p</i> -NO ₂
C-1	192.3	193.5	192.9	193.0	193.2	194.0	193.8	193.2	193.3	193.0	192.9
C-2	49.3	49.5	49.3	49.4	49.4	49.8	49.7	49.3	49.5	49.2	49.2
C-4	44.0	44.9	44.6	44.7	44.7	46.1	46.0	43.9	45.0	44.6	44.3
C-4a	155.1	154.3	142.1	156.4	153.9	153.0	154.3	146.9	142.8	154.6	151.7
C-5a	130.8	129.7	129.6	129.6	129.6	129.7	130.1	130.2	129.7	135.3	129.5
C-6	122.0	122.0	120.9	122.1	120.8	122.5	122.4	122.1	122.8	121.6	119.6
C-7	119.7	122.7	119.8	120.0	119.2	122.9	121.5	121.7	120.4	122.6	119.6
C-8	136.5	135.7	135.7	136.6	135.7	135.7	135.9	137.1	135.7	145.6	135.9
C-9	119.9	120.2	119.8	119.3	119.8	122.8	120.8	121.3	120.2	120.2	119.5
C-9a	138.9	138.2	138.3	139.0	138.3	138.4	138.3	139.5	138.3	147.4	138.4
C-11	54.0	56.9	56.1	53.0	56.9	57.3	58.0	55.4	56.6	56.2	55.9
C-11a	109.3	119.7	110.1	109.8	110.4	112.0	110.1	119.1	110.5	109.7	109.1
C-1'	133.3	133.6	132.0	132.0	132.1	132.1	132.5	132.2	132.2	137.9	131.9
C-2'	133.0	126.5	128.1	154.9	124.6	128.1	127.9	125.8	130.9	119.6	127.1
C-3'	126.3	127.3	127.6	120.7	153.9	113.7	126.9	127.9	128.7	127.9	122.6
C-4'	127.3	121.1	127.2	126.9	128.5	158.2	127.4	130.1	127.7	133.1	127.7
C-5'	129.3	125.1	127.6	127.7	119.8	113.7	133.1	128.0	128.7	128.5	122.6
C-6'	128.3	126.3	128.1	126.9	128.5	128.1	128.8	130.0	130.9	121.0	127.1
C-3(CH ₃)	27.4	27.5	27.7	27.4	27.0	27.7	28.0	27.3	27.4	27.1	27.3
OCH ₃	28.3	28.6	28.4	27.7	27.1	28.9	28.6	28.4	28.6	28.4	28.2
	-	-	-	55.0	54.4	55.1	-	-	-	-	-

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

ing at 125 MHz in deuteriochloroform solution containing tetramethylsilane as the internal standard with chemical shifts δ (ppm) expressed downfield from tetramethylsilane. The mass spectra were measured on a JEOL JMS-AC505 and JEOL MS-SX 102A high-resolution mass spectrometer with accurate mass determination of the molecular ion and the principal fragment ions, 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. Compounds **I** was prepared following methods developed by us, with modifications [12].

General Procedure for the Synthesis of the 11-[(*o*-; *m*-; and *p*-Substituted)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one, **II**, **1-11**.

A mixture of 1×10^{-3} mole of the 2-cyclohexenone **I**; 1×10^{-3} mole of corresponding (*o*-; *m*-; and *p*-substituted)benzaldehyde, 0.5 mL of acetic acid in 5.0 mL ethanol was heated at reflux for 1 hour and 45 minutes. The reaction mixture was cooled to room temperature and evaporated *in vacuo* to yield a semisolid. The residual semisolid was purified by crystallization from hexane-ethyl acetate to yield compounds **II**, **1-11**, in 61-90%.

11-[(*o*-Chloro)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**1**).

This compound was obtained as a brown solid in 83% yield; mp 210°; ir (chloroform): ν N-H 3413, C=O 1621, C-N 1367 and 1279, C-O 1391 and 1246 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.06 and 1.12 (s, 6H, $\text{C}_3\text{-CH}_3$), 2.04 (d, 1H, $J=16.5$ Hz, 2-Ha), and 2.18 (d, 1H, $J=15.9$ Hz, 2-Hb); 2.62 (s, 1H, $J=16.1$, 4-Ha); 2.63 (s, 1H, $J=16.3$ Hz, 4-Hb); 5.98 (s, 1H, 11-H); 6.48 (d, 1H, $J=8.4$ Hz, 6-H); 6.49 (dd, 1H, $J=2.1$, 8.7 Hz, 7-H); 6.56 (d, 1H, $J=2.4$ Hz, 9-H); 6.76 (dt, 1H, $J=1.8$; 7.5 Hz, 4'-H); 7.00 (dd, 1H, $J=1.2$, 7.0 Hz, 3'-H); 7.09 (dd, 1H, $J=1.8$, 8.0 Hz, 6'-H); 7.35 (dt, 1H, $J=1.2$, 7.6 Hz, 5'-H); 9.02 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 386 (M^+); 388 [$\text{M}+2$] $^+$; 390 [$\text{M}+4$] $^+$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}$: C, 65.12; H, 5.21; N, 7.23. Found: C, 65.00; H, 5.28; N, 7.33.

11-[(*m*-Chloro)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**2**).

This compound was obtained as a brown solid in 85% yield; mp 205°; ir (chloroform): ν N-H 3415; C=O 1618; C-N 1368 and 1280, C-O 1390 and 1248 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.07 and 1.13 (s, 6H, $\text{C}_3\text{-CH}_3$), 2.21 (d, 1H, $J=16.5$ Hz, 2-Ha); 2.30 (d, 1H, $J=16.2$ Hz, 2-Hb); 2.52 (d, 1H, $J=16.2$ Hz, 4-Ha); 2.59 (d, 1H, $J=16.0$ Hz, 4-Hb); 5.87 (s, 1H, 11-H), 6.40 (d, 1H, $J=8.5$ Hz, 6-H); 6.51 (d, 1H, $J=2.2$ Hz, 9-H); 6.55 (dd, 1H, $J=2.2$, 8.5 Hz, 7-H); 6.98 (dd, 1H, $J=1.8$, 9.0 Hz, 4'-H); 7.05 (dd, 1H, $J=1.8$, 9.0 Hz, 5'-H); 7.06 (dd, 1H, $J=1.2$, 9.0 Hz, 6'-H); 7.07 (d, 1H, $J=1.6$ Hz, 2'-H); 8.22 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 386 (M^+); 388 [$\text{M}+2$] $^+$; 390 [$\text{M}+4$] $^+$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}$: C, 65.12; H, 5.21, N, 7.23. Found: C, 65.22, H, 5.29; N, 7.13.

11-[(*p*-Chloro)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**3**).

This compound was obtained as a brown solid in 84% yield, mp 160°; ir (chloroform): ν N-H 3413, C=O 1619; C-N 1368 and 1287, C-O 1390 and 1245 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.08 and 1.12 (s, 6H, $\text{C}_3\text{-CH}_3$); 2.19 (d, 1H, $J=15.8$ Hz, 2-Ha), 2.30 (d, 1H, $J=16.3$ Hz, 2-Hb); 2.52 (d, 1H, $J=16.2$ Hz, 4-Ha);

2.60 (d, 1H, $J=16.0$ Hz, 4-Hb), 5.86 (s, 1H, 11-H); 6.41 (d, 1H, $J=8.4$ Hz, 6-H); 6.52 (d, 1H, $J=2.1$ Hz, 9-H); 6.62 (dd, 1H, $J=2.0$, 8.5 Hz, 7-H); 7.05 and 7.08 (AA'BB', 4H, $J=8.5$ Hz, phenyl protons of "D" ring), 8.47 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 386 (M^+); 388 [$\text{M}+2$] $^+$; 390 [$\text{M}+4$] $^+$.

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}$: C, 65.12, H, 5.21; N, 7.23. Found: C, 65.01; H, 5.12, N, 7.32.

11-[(*o*-Methoxy)-phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**4**).

This compound was obtained as a brown solid in 65% yield, mp 230°; ir (chloroform): ν N-H 3413, C=O 1618, C-N 1368 and 1270, C-O 1392 and 1249 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.08 and 1.13 (s, 6H, $\text{C}_3\text{-CH}_3$); 2.21 (d, 1H, $J=16.1$ Hz, 2-Ha); 2.25 (d, 1H, $J=16.1$ Hz, 2-Hb); 2.55 (d, 1H, $J=16.3$ Hz, 4-Ha); 2.56 (d, 1H, $J=16.3$ Hz, 4-Hb); 3.94 (s, 3H, -OCH₃), 6.13 (s, 1H, 11-H); 6.27 (d, 1H, $J=8.3$ Hz, 6-H); 6.34 (d, 1H, $J=2.0$ Hz, 9-H); 6.55 (dd, 1H, $J=2.1$, 8.6 Hz, 7-H); 6.62 (dt, 1H, $J=1.7$, 7.3 Hz, 4'-H); 6.67 (dd, 1H, $J=1.3$, 7.8 Hz, 3'-H); 6.81 (dd, 1H, $J=1.6$, 8.1 Hz, 6'-H); 7.05 (dt, 1H, $J=1.1$, 7.4 Hz, 5'-H); 8.31 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 382 (M^+); 384 [$\text{M}+2$] $^+$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_2$: C, 69.01; H, 6.06; N, 7.32. Found: C, 69.15, H, 6.14, N, 7.23.

11-[(*m*-Methoxy)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**5**).

This compound was obtained as a brownish solid in 75% yield; mp 220°; ir (chloroform) ν N-H 3414, C=O 1619; C-N 1368 and 1269, C-O 1393 and 1260 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.06 and 1.12 (s, 6H, $\text{C}_3\text{-CH}_3$), 2.20 (d, 1H, $J=16.2$ Hz, 2-Ha); 2.30 (d, 1H, $J=16.2$ Hz, 2-Hb); 2.50 (d, 1H, $J=16.2$ Hz, 4-Ha); 2.60 (d, 1H, $J=16.2$ Hz, 4-Hb). 3.65 (s, 3H, OCH₃), 5.87 (s, 1H, 11-H); 6.42 (d, 1H, $J=8.4$ Hz, 6-H); 6.51 (d, 1H, $J=2.2$ Hz, 9-H); 6.60 (dd, 1H, $J=2.1$, 8.4 Hz, 7-H); 6.63 (d, 1H, $J=2.1$ Hz, 2'-H); 6.70 (dd, 1H, $J=2.1$, 8.0 Hz, 5'-H); 7.02 (dd, 1H, $J=1.5$, 9.0 Hz, 6'-H); 7.05 (dd, 1H, $J=2.2$, 7.8 Hz, 4'-H); 8.35 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 382 (M^+); 384 [$\text{M}+2$] $^+$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_2$: C, 69.01; H, 6.06; N, 7.32. Found: C, 69.12; H, 5.98; N, 7.24.

11-[(*p*-Methoxy)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**6**).

This compound was obtained as a brown solid in 90% yield; mp 145°; ir (chloroform): ν N-H 3415; C=O 1616; C-N 1369 and 1263, C-O 1392 and 1235 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.08 and 1.14 (s, 6H, $\text{C}_3\text{-CH}_3$); 2.05 (d, 1H, $J=16.2$ Hz, H-2a); 2.21 (d, 1H, $J=16.2$ Hz, 2-Hb); 2.38 (d, 1H, $J=16.0$ Hz, 4-Ha); 3.31 (d, 1H, $J=16.0$ Hz, 4-Hb); 3.69 (s, 3H, -OCH₃); 5.86 (s, 1H, 11-H); 6.33 (d, 1H, $J=8.4$ Hz, 6-H); 6.44 (d, 1H, $J=1.8$ Hz, 9-H); 6.66 (dd, 1H, $J=1.9$, 8.7 Hz, 7-H); 6.67 and 6.96 (AA'BB', 4H, $J=9.0$ Hz, phenyl protons of "D" ring); 8.40 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 382 (M^+); 384 [$\text{M}+2$] $^+$.

Anal. Calcd. for $\text{C}_{22}\text{H}_{23}\text{ClN}_2\text{O}_2$: C, 69.01; H, 6.06; N, 7.32. Found: C, 68.93; H, 6.15; N, 7.39.

11-[(*o*-Bromo)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**7**).

This compound was obtained as a brown solid in 61% yield; mp 220°; ir (chloroform): ν N-H 3413, C=O 1618; C-N 1367 and 1270; C-O 1393 and 1242 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.06 and 1.13 (s, 6H, $\text{C}_3\text{-CH}_3$); 2.22 (d, 1H, $J=16.3$ Hz; 2-Ha);

2.31 (d, 1H, J=16.3 Hz, 2-Hb); 2.47 (d, 1H, J=16.0 Hz, 4-Ha); 2.48 (d, 1H, J=16.0 Hz, 4-Hb); 6.16 (s, 1H, 11-H); 6.36 (d, 1H, J=8.3 Hz, 6-H); 6.43 (d, 1H, J=2.0 Hz, 9-H); 6.61 (dd, 1H, J=2.1, 8.4 Hz, 7-H); 6.73 (dt, 1H, J=2.5, 7.6 Hz, 4'-H); 6.93 (dd, 1H, J=2.3, 8.0 Hz, 3'-H); 6.94 (dd, 1H, J=2.3, 9.0 Hz, 6'-H); 7.48 (dt, 1H, J=2.5, 9.0 Hz, 5'-H); 8.25 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 430 (M⁺); 432 [M+2]⁺; 434 [M+4]⁺.

Anal. Calcd. for C₂₁H₂₀ClBrN₂O: C, 58.42; H, 4.67; N, 6.49. Found: C, 58.30, H, 4.74; N, 6.41.

11-[(*m*-Bromo)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**8**).

This compound was obtained as a brownish solid in 76% yield, mp 228°; ir (chloroform): ν N-H 3413; C=O 1619; C-N 1368 and 1268; C-O 1392 and 1242 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 1.07 and 1.12 (s, 6H, C₃-CH₃); 2.01 (d, 1H, J=16.0 Hz, 2-Ha); 2.2 (d, 1H, J=16.0 Hz, 2-Hb); 2.57 (d, 1H, J=16.0 Hz, 4-Ha); 2.58 (d, 1H, J=16.0 Hz, 4-Hb); 5.67 (s, 1H, 11-H); 6.54 (d, 1H, J=8.4 Hz, 6-H); 6.60 (d, 1H, J=2.4 Hz, 9-H); 6.67 (dd, 1H, J=2.1, 8.4 Hz, 7-H); 7.05 (dd, 1H, J=2.1, 7.8 Hz, 5'-H); 7.06 (d, 1H, J=2.1 Hz, 2'-H); 7.11 (dd, 1H, J=1.8, 7.5 Hz, 4'-H); 7.12 (dd, 1H, J=1.6, 7.5 Hz, 6'-H); 8.91 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 430 (M⁺); 432 [M+2]⁺; 434 [M+4]⁺.

Anal. Calcd. for C₂₁H₂₀ClBrN₂O: C, 58.42; H, 4.67; N, 6.49. Found: C, 58.53; H, 4.75; N, 6.40.

11-[(*p*-Bromo)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**9**).

This compound was obtained as a brownish solid in 85% yield; mp 155°; ir (chloroform): ν N-H 3413, C=O 1618, C-N 1370 and 1272; C-O 1390 and 1250 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 1.06 and 1.12 (s, 6H, C₃-CH₃); 2.20 (d, 1H, J=15.8 Hz, 2-Ha); 2.30 (d, 1H, J=15.8, 2-Hb); 2.50 (d, 1H, J=16.8 Hz, 4-Ha); 2.58 (d, 1H, J=16.8 Hz, 4-Hb); 5.85 (s, 1H, 11-H); 6.38 (d, 1H, J=8.4 Hz, 6-H); 6.49 (d, 1H, J=2.2 Hz, 9-H); 6.64 (dd, 1H, J=2.1; 8.5 Hz, 7-H); 6.97 and 7.24 (AA'BB', 4H, J=8.5 Hz, phenyl protons of the "D" ring); 8.24 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 430 (M⁺); 432 [M+2]⁺; 434 [M+4]⁺.

Anal. Calcd. for C₂₁H₂₀ClBrN₂O: C, 58.42; H, 4.67; N, 6.49. Found: C, 58.54; H, 4.60; N, 6.58.

11-[(*m*-Nitro)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**10**).

This compound was obtained as a brown solid in 62% yield; mp 150, ir (chloroform): ν N-H 3411; C=O 1619; C-N 1351 and 1248; C-O 1392 and 1274 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 1.06 and 1.12 (s, 6H, C₃-CH₃); 2.22 (d, 1H, J=16.3 Hz, 2-Ha); 2.32 (d, 1H, J=16.2 Hz, 2-Hb); 2.43 (d, 1H, J=16.2 Hz, 4-Ha); 2.45 (d, 1H, J=16.2 Hz, 4-Hb); 5.99 (s, 1H, 11-H); 6.45 (d, 1H,

J=8.4 Hz, 6-H); 6.54 (d, 1H, J=2.3 Hz, 9-H); 6.62 (dd, 1H, J=2.4, 8.7 Hz, 7-H); 7.02 (d, 1H, J=2.3 Hz, 2'-H); 7.32 (dd, 1H, J=2.1, 7.9 Hz, 5'-H); 7.50 (dd, 1H, J=1.8, 7.7 Hz, 4'-H); 7.91 (dd, 1H, J=1.8, 8.1 Hz, 6'-H); 8.52 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 397 (M⁺); 399 [M+2]⁺.

Anal. Calcd. for C₂₁H₂₀ClN₃O₃: C, 63.39; H, 5.07; N, 10.56. Found: C, 63.49, H, 5.00; N, 10.64.

11-[(*p*-Nitro)phenyl]-8-chloro-3,3-dimethyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**11**).

This compound was obtained as a brown solid in 86% yield, mp 165; ir: ν N-H 3411, C=O 1620; C-N 1367 and 1251, C-O 1391 and 1246 cm⁻¹; ¹H-nmr (deuteriochloroform): δ 1.08 and 1.11 (s, 6H, C₃-CH₃); 2.18 (d, 1H, J=16.7 Hz, 2-Ha); 2.28 (d, 1H, J=16.2 Hz, 2-Hb); 2.61 (d, 1H, J=16.2 Hz, 4-Ha); 2.62 (d, 1H, J=16.2 Hz, 4-Hb); 5.92 (s, 1H, 11-H); 6.50 (d, 1H, J=8.4 Hz, 6-H); 6.61 (d, 1H, J=2.2 Hz, 9-H); 6.96 (dd, 1H, J=2.0, 9.0 Hz, 7-H); 7.32 and 7.96 (AA'BB'), 4H, J=8.6 Hz, phenyl protons of "D" ring); 8.80 (bs, 2H, N-H, deuterium oxide exchangeable); ms: m/z 397 (M⁺); 399 [M+2]⁺.

Anal. Calcd. for C₂₁H₂₀ClN₃O₃: C, 63.39; H, 5.07; N, 10.56. Found: C, 63.25; H, 5.17, N, 10.48.

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