Tricyclic Heteroaromatic Systems. 1,2,3,4-Tetrahydropyrazolo[4,3-*c*][1]benzazepin-1-ones as Potential Antitumor Agents

Giovanna Palazzino, Lucia Cecchi*, Vittoria Colotta, Fabrizio Melani, and Guido Filacchioni

Dipartimento di Scienze Farmaceutiche, Universita' di Firenze, Via Gino Capponi, 9, 50121 Firenze, Italy

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The synthesis of 1,2,3,4-tetrahydropyrazolo[4,3-*c*][1]benzazepin-1-ones **1** and that of its 10-methyl derivative **2** is reported. The preparation of the latter from 3-(2-aminobenzyl)-3-pyrazolin-5-one and triethyl orthoformate gave as the main product a derivative of the new tricyclic ring system, pyrazolo[1,5-*c*][1,3]benzodiazepine. The structures of the new compounds synthesized were assigned by means of a ^{13}C nmr study.

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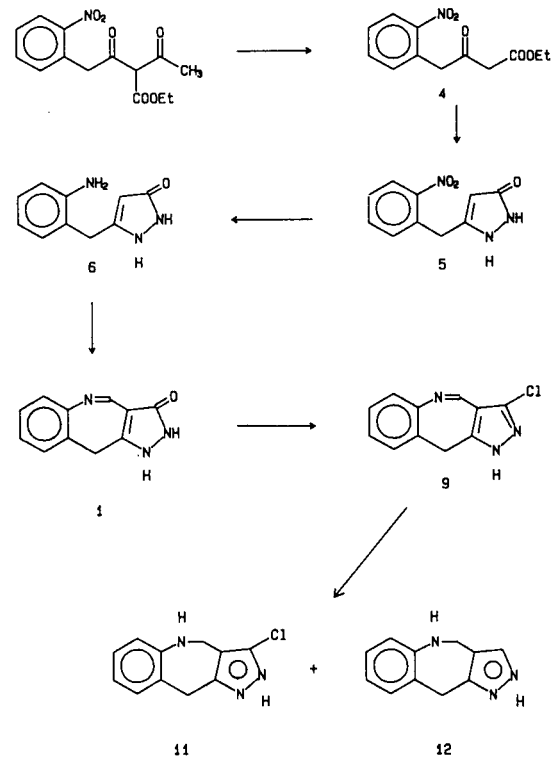
Since the discovery of the antitumor activity of the antibiotics anthramycin, tomaymycin and sibiromycin, whose common feature is the pyrrolo[2,1-*c*][1,4]benzodiazepine tricyclic ring system, a great deal of work has been carried out on six-seven-five fused ring systems [1]. The pyrrole ring has been displaced to all the four possible positions of the 1,4-benzodiazepine moiety, to discover that only the pyrrole derivatives fused at the 3,4-position of the 1,4-benzodiazepine moiety are important for their biological activity.

Thus, in the hope that chemical modification of the natural antibiotics would lead to products of biological interest, we reported the syntheses of some pyrazolo[5,1-*c*]-[1,4]benzodiazepine [2-3], pyrazolo[4,5-*c*]- and pyrazolo-[4,3-*c*][1]benzazepine derivatives [4-5]. Following up these papers we hereby report the synthesis of 1,2,3,4-tetrahydropyrazolo[4,3-*c*][1]benzazepin-1-one and that of its 10-methyl derivative **2**. Our synthesis work moreover yielded up a derivative of the new tricyclic ring system pyrazolo[1,5-*c*][1,3]benzodiazepine **3**.

By reacting ethyl 2-acetyl-3-oxo-4-(2-nitrophenyl)-butanoate [6] with ammonia in anhydrous ethanol, ethyl 3-oxo-4-(2-nitrophenyl)butanoate **4** was prepared. Compound **4** reacted with hydrazine hydrate to yield 3-(2-nitrobenzyl)-3-pyrazolin-5-one (**5**). Catalytic reduction of the latter gave rise to the 2-aminobenzyl derivative **6**. Allowing **6** to react with triethyl orthoformate, by direct cyclization, 1,2,3,4-tetrahydropyrazolo[4,3-*c*][1]benzazepin-1-one (**1**) was obtained (see Scheme 1).

The synthesis of its 10-methyl derivative **2** was achieved as outlined in Scheme 2. Allowing **5** to react with acetic anhydride, two products, namely 1-acetyl-5-(2-nitrobenzyl)-pyrazole-3-acetate (**7**) and 3-(2-nitrobenzyl)-4-acetyl-3-pyrazolin-5-one (**8**), were obtained. Compound **7** was discarded, while compound **8** was catalytically reduced to yield 1,2,3,4-tetrahydro-10-methylpyrazolo[4,3-*c*][1]benzazepin-1-one (**2**). Compound **2** was also obtained as the minor product by reacting **6** with triethyl orthoacetate.

Scheme 1

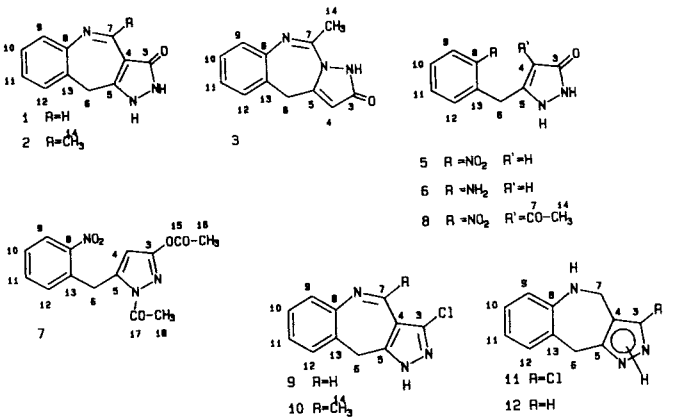


The main product of this reaction was the 2,4-dihydro-10-methyl-1*H*-pyrazolo[1,5-*c*][1,3]benzodiazepin-2-one (**3**). The latter is a derivative of the new tricyclic ring system pyrazolo[1,5-*c*][1,3]benzodiazepine as yet unreported in the literature.

Compounds **1** and **2** were moreover treated with phosphorus oxychloride to yield the 1-chloro derivatives **9** and **10**, respectively. Compound **9** was catalytically reduced to yield 2(3),4,9,10-tetrahydro-1-chloropyrazolo[4,3-*c*][1]benzazepine (**11**) as the main product, with a small amount of 2(3),4,9,10-tetrahydropyrazolo[4,3-*c*][1]benzazepine (**12**). Unfortunately this reaction took place with very low yield

Table 1

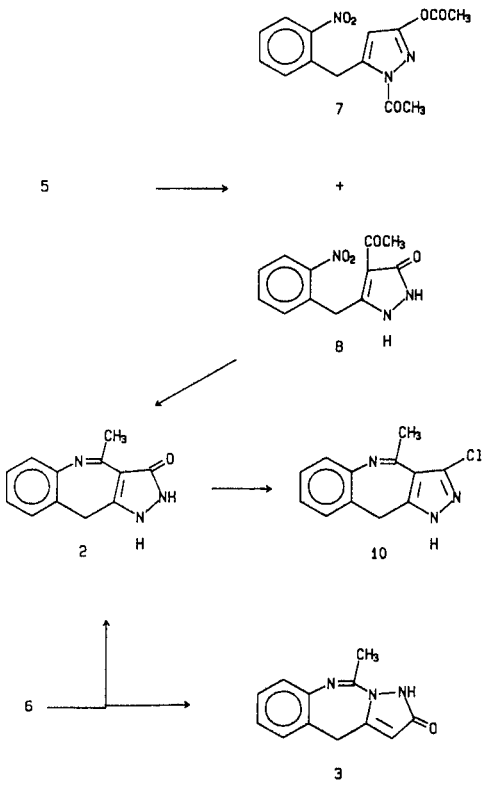
^{13}C Chemical Shift Assignments (ppm)



No.	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18
1	168.24	103.57	147.59	34.94	142.75	139.16	122.00	127.41	126.42	131.48	126.57					
2	168.26	101.00	147.29	34.79	159.88	139.01	122.16	127.09	126.33	130.30	128.24	18.37				
3	163.01	92.13	146.60 [a]	29.54	148.77 [a]	144.25	126.08 [b]	127.48 [b]	126.29 [b]	128.06 [b]	130.58	23.99				
5	160.25	88.73	141.92	29.35		148.79	124.58	128.10	133.54	132.07	133.34					
6	160.75	89.04	143.18	28.15		146.08	114.92	127.23	116.53	129.29	122.76					
7	155.82	103.47	145.69	31.07		148.78	124.80	128.41	133.77	131.76	131.96		170.65	22.90 [b]	167.64	20.50 [b]
8	160.55	104.52	145.36	29.58	192.20	149.09	124.44	127.82	133.39	131.17	132.48	29.08				
9	145.96	111.08	136.78	30.24	149.66	146.61	127.39	128.51	127.39	129.46	129.03					
10	145.81	111.25	135.66	29.80	157.84	146.44	126.66 [b]	127.16 [b]	125.98 [b]	128.56	129.27	27.01				
11	139.17 [c]	111.71	135.51 [c]	29.82 [c]	42.93	149.07	121.95 [b]	127.70 [b]	122.46 [b]	128.92 [b]	131.59					
12	NR	114.82	NR	31.33 [c]	42.98	149.30	120.80	127.20	121.48	129.10	131.10					

[a,b] The assignments may be reversed. [c] Broad signals.

Scheme 2



and any attempt to reduce compound **12** to the fundamental pyrazolo[4,3-*c*][1]benzazepine yielded a mixture of degradation products. Thus we were deterred from trying this same reaction on compound **10**.

The structures of all the synthesized compounds were assigned by a ^{13}C nmr study. In fact neither the ir nor the ^{1}H nmr spectra were very useful since the behaviour of the compounds synthesized in the solid state (ir) and in solution was quite different, giving rise to contrasting interpretations. The ir spectra in solution of the synthesized compounds were impossible due to their low solubility in organic solvents.

In Table 1 the ^{13}C nmr chemical shifts of the synthesized compounds are listed. An arbitrary numbering is used to identify all carbon atoms. The assignments are established as follows. Compounds **5-6, 8** exist in the ^{13}C nmr spectra in the 3-pyrazolin-5-one form and not in the corresponding pyrazol-3-olo form. These findings on the spectral data in solution are in agreement with the literature data [7] while the behaviour of compounds **5-6, 8** in the solid state are in disagreement with them [7]. However the ir spectra of compounds **5-6, 8** in nujol mull do not show any stretching band for the NH and C=O group, as reported in the literature for a similar compound, while they show a large broad band between 3000 and 2400 cm^{-1} due to the NH_2^+ group and an absorption band at about 1620 cm^{-1} due to the $C\text{-}O^-$. In the ^{13}C nmr spectra the existence of compounds **5-6** in the 5-one form is shown by the following data. The C-3 of compounds **5-6** is strongly deshielded (about 160 ppm) and in the coupled spectra it appears as a doublet because of its long range coupling constant with the C-4 proton ($^{3}J_{C3H4}$ = 3.8 Hz). On the other hand the C-4 is shielded at about 89 ppm because of the presence of the near C=O group and in the coupled spectrum it appears as a doublet of a triplet because of its long coupling constant with its own proton ($^{1}J_{C4H4}$ = 174.1 Hz) and with the C-6 protons ($^{3}J_{C4H6}$ = 3.4 Hz). The behaviour of the C-5 is characteristic in the coupled spectrum, where it appears as a quartet. This quartet is due to the fact that the C-5 coupled, with the same coupling constants, both with the C-4 proton ($^{2}J_{C5H4}$ = 7.1 Hz doublet) and with the C-6 protons ($^{2}J_{C5H6}$ = 7.1 Hz triplet), thus producing a quartet.

The structure of compound **7** was assigned as follows. The fact that one of the acetyl groups is at the oxygen atom is shown both by the ir spectrum ($OCOCH_3$ = 1770 cm^{-1}) and by the ^{13}C spectrum where the C-3 is more deshielded (155.82 ppm) than the C-3 of compounds **5-6**. These data are supported by the deshielded value of the C-4 (103.47 ppm). The other acetyl group is at a nitrogen atom. In fact the C-4 in the coupled spectrum appears as a doublet of a triplet because of its coupling constants with its own proton ($^{1}J_{C4H4}$ = 183.6 Hz) and with the C-6 protons ($^{3}J_{C4H6}$ = 3.8 Hz).

The structure of compound **8** ensued from the comparison of its ^{13}C nmr spectrum and those of compounds **5-7**. The C-3 shows the same downfield value as compounds **5-6** (160.55 ppm). The C-5 in the coupled spectrum appears as a triplet because of its sole coupling with the C-6 protons. These data and the deshielded value of the C-4 (104.52 ppm) demonstrated that the C-4 is a quaternary atom carrying an acetyl group.

The cyclization of compounds **6** and **8** to compounds **1** and **2** respectively, ensued in a more deshielded value of the C-3 (168 ppm) and of the C-5 (147 ppm). In both compounds **1** and **2** the C-4 is a quaternary atom (102 ppm) and in the coupled spectra it appears as a multiplet. In fact the C-4 of compound **1** coupled both with the C-6 and the C-7 protons while that of compound **2** coupled both with the C-6 and the C-14 protons. The C-7 chemical shift value of compound **1** is different from that of compound **2**. In fact in compound **1** the C-7 is at 142.75 ppm and it coupled with its own proton, while in compound **2** the C-7, being a quaternary atom, is more deshielded (159.88 ppm) and in the coupled spectrum appears as a quartet because of its coupling with the methyl protons ($^{2}J_{C7H14}$ = 6.0 Hz).

The structure of compound **3** ensued from a comparison of the chemical shift values of its C-3, C-4 and C-7 with those of the same carbon atoms of compound **2**. The chemical shift values of the C-3, C-4 and C-7 of compound

3 are all more upfield than the corresponding carbon atoms of compound **2**. The chemical shift of the C-4 (92.13 ppm) in compound **3** was no longer a quaternary atom as it has been in compound **2**, so that in the coupled spectrum it appears as a doublet of a triplet because of its coupling with its own proton ($^1J_{C4H4}$ = 178 Hz doublet) and with the C-6 protons ($^3J_{C4H6}$ = 2.8 Hz triplet). The structure of compound **3** is further confirmed by the behaviour of the C-5 in the coupled spectrum. In the latter the C-5 appears as a quartet because of its coupling both with the C-6 and the C-4 protons.

It should be noted that a coupling constant between the C-3 or the C-5 and the hydrogen at the pyrazole nitrogen was not observed in any compound.

In compounds **9-12** the C=O group is no longer present and the pyrazole moiety is aromatic. Thus all the absorption bands over 160 ppm have disappeared and the chemical shifts of the pyrazole carbon atoms are those characteristic of a substituted pyrazole [8].

Furthermore we should like to point out the tautomeric behaviour of the hydrogen of the pyrazole nitrogen of compounds **11-12**, which is revealed by the enlargement of the C-3, C-4 and C-5 signals, and may be due to the absence of the double bond in position 9-10, which, in the case of compounds **9-10**, stabilized the hydrogen at the pyrazole nitrogen by conjugation, giving rise to non tautomeric compounds.

EXPERIMENTAL

All melting points were determined on a Gallenkamp capillary melting point apparatus and are uncorrected. The ir spectra were recorded in nujol mull with a Perkin Elmer 1420 spectrophotometer. The ^{1}H nmr spectra were recorded with a Varian EM-360 instrument, chemical shifts are reported in δ (ppm) downfield from internal tetramethylsilane. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck, 70-230 mesh) were used for analytical and column chromatography. The natural abundance ^{13}C nmr spectra were run on a Varian FT-80A spectrometer at 20 MHz in the Fourier transform mode. All samples were recorded in 10 mm o.d. tubes at the probe temperature (45°) with concentrations of approximately 10% w/v in DMSO-d_6 which provided the deuterium signal for the field frequency lock. Chemical shifts were measured relative to the central peak of the solvent (DMSO-d_6 = 39.5 ppm) and corrected to internal tetramethylsilane. Typical acquisition parameters included: a spectral width of 5000 Hz, a flip angle of 42° and an interpulse delay between acquisitions of 510 μseconds. Chemical shift values were reproducible to better than ±0.05 ppm. The decoupled spectra were obtained without pulse delay and with a digitization of 2 points per cycle. The coupled spectra with nuclear Overhauser effect (nOe) were obtained putting the decoupler on during a pulse delay of 1.6 seconds and off during an acquisition time of 0.8 seconds. The digitization of the coupled spectra was 1.6 points per cycle.

Ethyl 3-Oxo-4-(2-nitrophenyl)butanoate (**4**).

A suspension of ethyl 2-acetyl-3-oxo-4-(2-nitrophenyl)butanoate [6] (17 g, 5.8 mmoles) in anhydrous ethanol (200 ml) was stirred under ammonia flow at 0° for two hours. The ammonia flow was stopped and the solution was stirred at room temperature for another two hours. The solution was brought to low volume under reduced pressure and the resulting solid was collected by suction and recrystallized from ethanol, mp 50-52°, 65% yield; ir: 1730, 1720, 1520, 1340 cm^{-1}; ^{1}H nmr (deuteriochloroform): 8.2-8.0 (m, 1H, benzene proton), 7.7-7.2 (m, 3H, benzene protons), 4.28 (s, 2H, CH_2), 4.20 (q, 2H, CH_2), 3.61 (s, 2H, 4-CH_2), 1.29 (t, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{13}NO_5$: C, 57.37; H, 5.22; N, 5.58. Found: C, 57.61; H, 5.27; N, 5.72.

3-(2-Nitrobenzyl)-3-pyrazolin-5-one (**5**).

A solution of **4** (9 g, 36.1 mmoles) and 98% hydrazine hydrate (2.2 g, 41.3 mmoles) in ethanol (20 ml) was stirred at room temperature for three hours. The resulting solid was collected by suction, washed with cold ethanol and recrystallized from ethanol, mp 187-189°, 87% yield; ir: 3000-2300, 1620, 1540, 1350 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 9.7 (br s, 2H, 2NH), 8.1-7.8 (m, 1H, benzene proton), 7.7-7.2 (m, 3H, benzene protons), 5.19 (s, 1H, H-4 proton), 4.17 (s, 2H, CH_2).

Anal. Calcd. for $C_{10}H_9N_3O_3$: C, 54.80; H, 4.14; N, 19.17. Found: C, 55.02; H, 4.37; N, 19.35.

3-(2-Aminobenzyl)-3-pyrazolin-5-one (**6**).

To a warm solution of **5** (1.5 g, 6.8 mmoles) in ethanol (200 ml) 10% Pd/C (0.6 g) was added. The mixture was hydrogenated in a Parr apparatus at 40 psi for 12 hours. The catalyst was filtered off and the solution was evaporated under reduced pressure to give a residue which was recrystallized from ethanol, mp 168-170°, 78% yield; ir: 3440, 3360, 3000-2200, 1620 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 10.3 (br s, 2H, 2NH), 7.0-6.3 (m, 4H, benzene protons), 5.22 (s, 1H, H-4 pyrazoline), 4.8 (br s, 2H, NH_2), 3.63 (s, 2H, CH_2).

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.48; H, 5.86; N, 22.21. Found: C, 63.42; H, 5.95; N, 22.60.

1,2,3,4-Tetrahydropyrazolo[4,3-*c*][1]benzazepin-1-one (**1**).

To a suspension of **6** (0.35 g, 1.8 mmoles) in toluene (30 ml) a solution of triethyl orthoformate (0.73 ml, 4.4 mmoles) in toluene (10 ml) was added, dropwise and under stirring. The mixture was refluxed for 1-2 hours. The solvents were distilled off under reduced pressure. The yellow solid mass was recrystallized from ethanol, mp >300°, 73% yield; ir: 3400-2600, 1660 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 10.7 (br s, 2H, 2NH), 7.62 (s, 1H, H-10), 7.73 ("s", 4H, benzene protons), 3.90 (s, 2H, CH_2).

Anal. Calcd. for $C_{11}H_9N_3O$: C, 66.32; H, 4.55; N, 21.09. Found: C, 66.07; H, 4.67; N, 20.72.

1-Acetyl-5-(2-nitrobenzyl)pyrazole-3-acetate (**7**).

A mixture of **5** (1 g, 4.6 mmoles) and anhydrous sodium acetate (0.38 g, 4.6 mmoles) in acetic anhydride (4.5 ml) was refluxed at 110° for 45 minutes. To the cooled solution water (20 ml) was added. The aqueous solution was extracted three times with diethyl ether (20-30 ml each time). The two layers were separated. The aqueous layer, which contained compound **8**, was left aside. The organic layer was dried over anhydrous sodium sulfate and brought to dryness under reduced pressure. The residue was chromatographed on a silica gel column (eluting system cyclohexane/ethyl acetate, 1:1). The title compound was recovered from the first eluates and recrystallized from cyclohexane/ethyl acetate, mp 89-90°, 28% yield; ir: 1770, 1740, 1730, 1525, 1340 cm^{-1}; ^{1}H nmr (deuteriochloroform): 8.2-7.9 (m, 1H, benzene proton), 7.7-7.2 (m, 3H, benzene protons), 5.98 (s, 1H, H-4), 4.70 (s, 2H, CH_2), 2.61 (s, 3H, CH_3), 2.30 (s, 3H, CH_3).

Anal. Calcd. for $C_{14}H_{13}N_3O_5$: C, 55.43; H, 4.32; N, 13.85. Found: C, 55.48; H, 4.34; N, 13.78.

3-(2-Nitrobenzyl)-4-acetyl-3-pyrazolin-5-one (**8**).

The title compound was contained in the aqueous layer of the synthesis of compound **7**. The aqueous layer was allowed to stand for one week. The resulting white precipitate was collected by suction and recrystallized from ethanol, mp 214-216°, 26% yield; ir: 3200-2400, 1640, 1630, 1520, 1350 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): 8.2-7.9 (m, 1H, benzene proton), 7.3-7.0 (m, 3H, benzene protons), 4.30 (s, 2H, CH_2), 2.30 (s, 3H, CH_3).

Anal. Calcd. for $C_{13}H_{11}N_3O_4$: C, 55.16; H, 4.25; N, 16.09. Found: C, 55.22; H, 4.33; N, 15.89.

1,2,3,4-Tetrahydro-10-methylpyrazolo[4,3-*c*][1]benzazepin-1-one (**2**).

Method A.

To a warm solution of **8** (0.360 g, 1.4 mmoles) in ethanol (100 ml) 10% Pd/C (0.1 g) was added. The mixture was hydrogenated in a Parr apparatus at 20 psi for 8 hours. The catalyst was filtered off and the solution was evaporated at reduced pressure to give a residue which was chromatographed on a silica gel column (eluting system chloroform/methanol, 8:2). The title compound was recovered from the evaporation of the first eluates, 50% yield.

Method B.

To a solution of **6** (2 g, 10.6 mmoles) in toluene (30 ml) triethyl orthoacetate (3.8 ml, 21.1 mmoles) was added, dropwise and under stirring. The mixture was refluxed for 1 hour and 30 minutes. The solvents were distilled off under reduced pressure and the residue was chromatographed on a silica gel column with two different eluting systems: a) cyclohexane/ethyl acetate, 4:6; from the evaporation of the central eluates compound **3** was recovered. b) chloroform/methanol, 9:1; from the evaporation of the central eluates the title compound was recovered; mp 315-316° (from dimethyl formamide), 10% yield; ir: 3400-2600, 1660 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): 10.5 (br s, 1H, NH), 10.3 (br s, 1H, NH), 7.30 ("s", 4H, benzene protons), 3.75 (s, 2H, CH_2), 2.62 (s, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{11}N_3O$: C, 67.57; H, 5.20; N, 19.70. Found: C, 67.32; H, 5.27; N, 20.01.

2,4-Dihydro-10-methyl-1*H*-pyrazolo[1,5-*c*][1,3]benzodiazepin-2-one (**3**).

The title compound was obtained as described in Method B of the synthesis of compound **2**, mp >300°, 20% yield; ir: 3200-2400, 1650, 1600 cm^{-1}; ^1H nmr (deuteriochloroform): 7.5-7.1 (m, 4H, benzene protons), 5.60 (s, 1H, H-3), 3.78 (s, 2H, CH_2), 2.66 (s, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{11}N_3O$: C, 67.57; H, 5.20; N, 19.70. Found: C, 67.32; H, 5.21; N, 19.76.

3,4-Dihydro-1-chloropyrazolo[4,3-*c*][1]benzazepine (**9**).

A suspension of **1** (0.6 g, 3.0 mmoles) in phosphorus oxychloride (10 ml) was refluxed for 1 hour and 30 minutes. The cooled solution was poured into ice and neutralized with sodium carbonate. The resulting light yellow solid was collected by suction and purified by dissolving it in 6 *N* hydrochloric acid and precipitating it with sodium carbonate, mp 218-220°, 46% yield; ir: 3200-2500, 1610 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): 13.4 (br s, 1H, NH), 8.42 (s, 1H, H-10), 7.30 ("s", 4H, benzene protons), 3.92 (s, 2H, CH_2).

Anal. Calcd. for $C_{11}H_8ClN_3$: C, 60.70; H, 3.70; N, 19.30. Found: C, 60.72; H, 3.75; N, 18.90.

3,4-Dihydro-1-chloro-10-methylpyrazolo[4,3-*c*][1]benzazepine (**10**).

The title compound was prepared from **2** as described in the preparation of **9**. The neutralized solution was extracted three times with ethyl acetate (80-90 ml each time). The dried organic solvent (sodium sulfate) was evaporated under reduced pressure to give a residue which was recrystallized from ethanol/water, mp 200-202°, 80% yield; ir: 3200-2400, 1600 cm^{-1}; ^1H nmr (deuteriochloroform): 7.4-7.0 (m, 4H, benzene protons), 3.82 (s, 2H, CH_2), 2.70 (s, 3H, CH_3).

Anal. Calcd. for $C_{12}H_{10}ClN_3$: C, 62.20; H, 4.36; N, 18.14. Found: C, 62.00; H, 4.47; N, 18.22.

2(3),4,9,10-Tetrahydro-1-chloropyrazolo[4,3-*c*][1]benzazepine (**11**).

To a solution of **9** (0.73 g, 3.3 mmoles) in glacial acetic acid (20 ml) 10% Pd/C (0.08 g) was added. The mixture was hydrogenated at atmospheric pressure for 4 hours and then allowed to stand overnight. The catalyst was filtered off and the solution was concentrated to a low volume under reduced pressure. The solution was diluted with water and neutralized with sodium carbonate. The solution was extracted three times with ethyl acetate (50 ml each time) and the organic layer was washed with water. The dried organic layer (sodium sulfate) was evaporated under reduced pressure and the residue was chromatographed on a silica gel column (eluting system chloroform/acetonitrile, 7:3). The title compound was recovered from the evaporation of the first eluates and recrystallized from cyclohexane/ethyl acetate, mp 173-174°, 32% yield; ir: 3270-3140, 3080 cm^{-1}; ^1H nmr (deuteriochloroform): 7.3-6.9 (m, 4H, benzene protons), 4.10 (s, 4H, 2 CH_2).

Anal. Calcd. for $C_{11}H_{10}ClN_3$: C, 60.13; H, 4.60; N, 19.13. Found: C, 60.22; H, 4.55; N, 19.05.

2(3),4,9,10-Tetrahydropyrazolo[4,3-*c*][1]benzazepine (**12**).

The title compound was obtained as described in the preparation of compound **11** by eluting the silica gel column with chloroform/methanol, 8:2, mp 172-173° (from methanol/water), 20% yield; ir: 3340, 3300, 3200-3060 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): 7.4-6.7 (m, 5H, 4 benzene protons + H-1), 4.28 (s, 2H, CH_2), 4.10 (s, 2H, CH_2).

Anal. Calcd. for $C_{11}H_{11}N_3$: C, 71.31; H, 5.29; N, 22.68. Found: C, 70.96; H, 5.94; N, 22.50.

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