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SPATIAL CONFIGURATION OF DERIVATIVES OF 5,5a,6,7-TETRAHYDROPYRIDO-[1,2-*a*]BENZIMIDAZOLE AND 6,7-DIHYDRO-5aH-PYRIDO-[1,2-*b*]BENZOXAZOLE

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The spatial configurations of 7,9-diphenyl-5a,6-tetramethylene-5,5a,6,7-tetrahydropyrido[1,2-a]-benzimidazole and 7,9-diphenyl-5a,6-tetramethylene-2,5a,6,7-tetrahydropyrido[1,2-a]benzimidazol-2-one have been established by X-ray crystallography. Analogous configurations are proposed for a series of other derivatives of 5,5a,6,7-tetrahydropyrido[1,2-a]benzimidazoles and some derivatives of 6,7-dihydro-5aH-pyrido[1,2-b]benzoxazoles on the basis of ^{1}H NMR spectroscopic data and the results of quantum chemical calculations using the MNDO, AM1, and PM3 methods.

Keywords: pyrido[1,2-*a*]benzimidazoles, pyrido[1,2-*b*]benzoxazoles, X-ray crystallographic analysis, quantum-chemical calculations.

Derivatives of 5,5a,6,7-tetrahydropyrido[1,2-*a*]benzimidazole (**1, 3, 5, 7, 9**) and 6,7-dihydro-5aH-pyrido[1,2-*b*]benzoxazole (**2, 4, 6, 8**) are formed by the reaction of 1,5-diketones with *o*-phenylenediamine and *o*-aminophenol respectively [1, 2].

Derivatives of 5,5a,6,7-tetrahydropyrido[1,2-*a*]benzimidazol-2-one (**10-14**) were obtained by oxidation of the corresponding 5,5a,6,7-tetrahydropyrido[1,2-*a*]benzimidazoles [3]. In the ^{1}H NMR spectra of all of these compounds, except the 5,5a,6,7-tetrahydropyrido[1,2-*a*]benzimidazoles **9** and **14**, a shift of the signal of one of the aromatic protons (a quinoid proton in compounds **10-13**) to high field was observed (Table 1). This signal is assigned to proton 1-H, which is close to the aromatic ring bonded to position 9. From an examination of models taking into account this assignment *cis* coupling of the tetrahydropyridine (A) and azoline (B) rings with a pseudoaxial position of the $N_{(10)}$–$C_{(10a)}$ bond relative to ring A is proposed. This in its turn assumes *cis* coupling of the tetrahydropyridine and the alicyclic side chain units (e.g., A/D coupling in compounds **3** and **11**). These same proposals were suggested previously for the configuration of the products of the reactions of *o*-carboxyl substituted hemicyclic 1,5-diketones with *o*-aminophenol and *o*-phenylenediamine [4].

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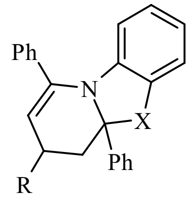
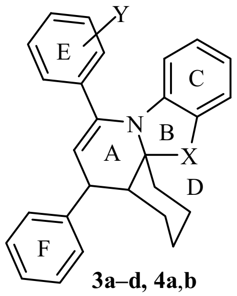
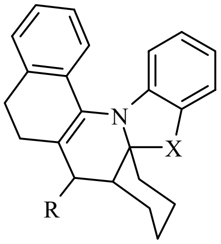


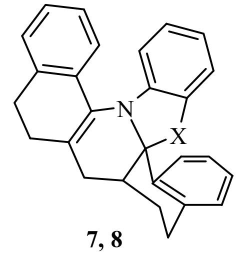
1a,**b**, **2**



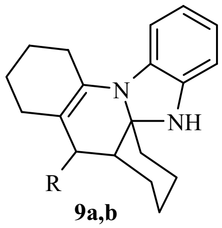
3a–d, **4a**,**b**



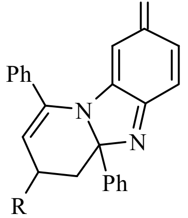
5, **6a**,**b**



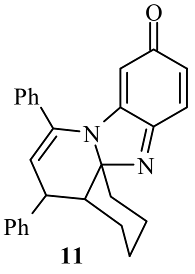
7, **8**



9a,**b**



10a,**b**



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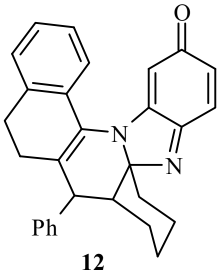

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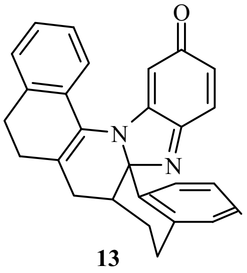

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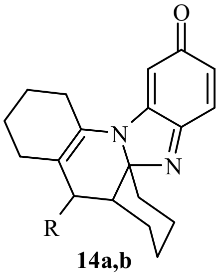

14a,**b**

1, **3**, **5**, **7** X = NH; **2**, **4**, **6**, **8** X = O; **1**, **6**, **9**, **10**, **14** **a** R = H; **b** R = Ph; **3**, **4** **a** Y = H; **b** Y = *p*-OCH_3; **c** Y = *p*-NO_2; **d** Y = *o*-NO_2; **2** R = H; **5** R = Ph

TABLE 1. Chemical Shifts (δ, ppm) for the $H_{(1)}$ Protons in Compounds **1-14**

Compound	δ*	Compound	δ*	Compound	δ*[2]
1a	5.81	**4b**	5.75	**10a**	4.85
1b	5.91	**5**	6.09	**10b**	4.94
2	5.81	**6a**	6.11	**11**	4.76
3a	5.65	**6b**	6.19	**12**	5.25
3b	5.70	**7**	6.15	**13**	5.30
3c	5.63	**8**	6.30	**14a**	5.74
3d	5.34	**9a**	6.60	**14b**	5.83
4a	5.71	**9b**	6.65		

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* Doublet with $J_{1,2}$ of the order of 7 Hz.

*[2] Doublet with $J_{1,3}$ of the order of 2 Hz.

We have carried out X-ray crystallographic analysis of compounds **3a** and **11** to determine more precisely their spacial configurations. X-ray crystallographic data on the bond lengths, valence and endocyclic torsion angles, and atomic coordinates are given in Tables 2-9 and the configuration of the molecules of compound **11** in the crystal is shown in Fig. 1 (only the molecule of compound **11** is shown in Fig. 1 because of the insignificant differences in the overall shape of the molecules of compounds **3a** and **11**).

The tetrahydropyridine ring A in both compounds has the $C_{(5a)}$ chair configuration; the imidazole ring B in compound **3a** has the envelope configuration at $C_{(5a)}$ ($C_{(5a)}$ is 0.163 Å out of the plane of mean plane of the ring); in compound **11**, ring B is almost planar with $N_{(10)}$ 0.04 Å out of the mean plane of the ring. Ring C is completely planar in compound **3a** and almost planar in compound **11** (the maximum deviation of $C_{(4a)}$ from the mean plane of the ring is 0.027 Å).

TABLE 2. Bond Lengths (*d*) in the Molecule of Compound **3a** and Their Least Squared Deviation (σ, Å) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	*d*, Å			
	PCA	MNDO	AM1	PM3
$C_{(1)}$–$C_{(2)}$	1.401	1.41	1.40	1.40
$C_{(1)}$–$C_{(10a)}$	1.379	1.40	1.39	1.39
$C_{(2)}$–$C_{(3)}$	1.384	1.40	1.39	1.39
$C_{(3)}$–$C_{(4)}$	1.378	1.41	1.40	1.40
$C_{(4)}$–$C_{(4a)}$	1.360	1.40	1.39	1.39
$N_{(5)}$–$C_{(4a)}$	1.399	1.43	1.42	1.44
$N_{(5)}$–$C_{(5a)}$	1.493	1.50	1.51	1.52
$C_{(6)}$–$C_{(5a)}$	1.524	1.58	1.56	1.55
$C_{(6)}$–$C_{(7)}$	1.563	1.57	1.53	1.54
$C_{(6)}$–$C_{(1')}$	1.538	1.55	1.52	1.53
$C_{(7)}$–$C_{(8)}$	1.522	1.51	1.48	1.49
$C_{(7)}$–$C_{(1''')}$	1.520	1.53	1.50	1.51
$C_{(8)}$–$C_{(9)}$	1.322	1.36	1.36	1.34
$C_{(9)}$–$N_{(10)}$	1.443	1.42	1.41	1.44
$C_{(9)}$–$C_{(1'')}$	1.498	1.49	1.48	1.48
$N_{(10)}$–$C_{(5a)}$	1.485	1.50	1.52	1.53
$N_{(10)}$–$C_{(10a)}$	1.421	1.42	1.42	1.44
$C_{(10a)}$–$C_{(4a)}$	1.411	1.43	1.44	1.41
$C_{(1')}$–$C_{(2')}$	1.525	1.54	1.51	1.52
$C_{(2')}$–$C_{(3')}$	1.514	1.54	1.51	1.52
$C_{(3')}$–$C_{(4')}$	1.526	1.54	1.51	1.52
$C_{(4')}$–$C_{(5a)}$	1.535	1.57	1.55	1.54
$C_{(1'')}$–$C_{(2'')}$	1.411	1.42	1.40	1.40
$C_{(1'')}$–$C_{(6'')}$	1.376	1.42	1.40	1.40
$C_{(2'')}$–$C_{(3'')}$	1.387	1.41	1.39	1.39
$C_{(3'')}$–$C_{(4'')}$	1.356	1.41	1.39	1.39
$C_{(4'')}$–$C_{(5'')}$	1.412	1.40	1.39	1.39
$C_{(5'')}$–$C_{(6'')}$	1.383	1.41	1.39	1.39
$C_{(1''')}$–$C_{(2''')}$	1.393	1.42	1.40	1.40
$C_{(1''')}$–$C_{(6''')}$	1.391	1.42	1.40	1.40
$C_{(2''')}$–$C_{(3''')}$	1.386	1.41	1.39	1.39
$C_{(3''')}$–$C_{(4''')}$	1.369	1.40	1.39	1.39
$C_{(4''')}$–$C_{(5''')}$	1.369	1.40	1.39	1.39
$C_{(5''')}$–$C_{(6''')}$	1.387	1.41	1.39	1.39
σ	0.008	0.03	0.02	0.02

TABLE 3. Valence Angles (ω) in the Molecule of Compound **3a** and Their Least Squares Deviation (σ, deg) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	ω, deg.			
	PCA	MNDO	AM1	PM3
$C_{(1)}-C_{(2)}-C_{(3)}$	120.9	122	121	121
$C_{(1)}-C_{(10a)}-C_{(4a)}$	121.0	120	120	121
$C_{(2)}-C_{(3)}-C_{(4)}$	121.3	121	121	121
$C_{(3)}-C_{(4)}-C_{(4a)}$	118.6	118	118	118
$C_{(4)}-C_{(4a)}-N_{(5)}$	130.3	128	128	128
$C_{(4a)}-N_{(5)}-C_{(5a)}$	107.9	108	106	107
$N_{(5)}-C_{(5a)}-C_{(4')}$	110.3	107	109	109
$C_{(5a)}-C_{(6)}-C_{(1')}$	110.7	112	111	111
$C_{(5a)}-C_{(4')}-C_{(3')}$	110.6	114	112	112
$C_{(6)}-C_{(5a)}-N_{(10)}$	110.8	112	113	112
$C_{(6)}-C_{(5a)}-N_{(5)}$	110.8	112	111	112
$C_{(6)}-C_{(5a)}-C_{(4')}$	112.2	112	110	112
$C_{(6)}-C_{(7)}-C_{(8)}$	110.9	114	112	113
$C_{(6)}-C_{(7)}-C_{(1''')}$	110.1	113	111	110
$C_{(6)}-C_{(1')}-C_{(2')}$	113.5	116	114	111
$C_{(7)}-C_{(6)}-C_{(5a)}$	111.6	113	112	111
$C_{(7)}-C_{(6)}-C_{(1')}$	110.2	113	111	110
$C_{(7)}-C_{(8)}-C_{(9)}$	125.2	126	124	124
$C_{(7)}-C_{(1''')}-C_{(2''')}$	120.9	120	120	120
$C_{(7)}-C_{(1''')}-C_{(6''')}$	120.5	122	121	121
$C_{(8)}-C_{(7)}-C_{(1''')}$	110.7	110	111	110
$C_{(8)}-C_{(9)}-N_{(10)}$	121.4	120	123	122
$C_{(8)}-C_{(9)}-C_{(1'')}$	122.7	122	118	120
$C_{(9)}-N_{(10)}-C_{(5a)}$	115.4	120	118	117
$C_{(9)}-N_{(10)}-C_{(10a)}$	120.3	125	122	121
$C_{(9)}-C_{(1'')}-C_{(2'')}$	118.8	121	120	120
$C_{(9)}-C_{(1'')}-C_{(6'')}$	121.6	121	121	121
$N_{(10)}-C_{(5a)}-N_{(5)}$	100.1	104	107	104
$N_{(10)}-C_{(5a)}-C_{(4')}$	112.2	109	108	108
$N_{(10)}-C_{(9)}-C_{(1'')}$	115.6	118	118	117
$N_{(10)}-C_{(10a)}-C_{(1)}$	131.7	132	130	130
$N_{(10)}-C_{(10a)}-C_{(4a)}$	107.2	108	110	109
$C_{(10a)}-C_{(1)}-C_{(2)}$	117.2	118	119	118
$C_{(10a)}-C_{(4a)}-C_{(4)}$	120.9	122	121	122
$C_{(10a)}-C_{(4a)}-N_{(5)}$	108.8	110	111	111
$C_{(10a)}-N_{(10)}-C_{(5a)}$	108.2	110	106	107
$C_{(1')}-C_{(2')}-C_{(3')}$	111.9	115	112	111
$C_{(2')}-C_{(3')}-C_{(4')}$	112.4	114	112	111
$C_{(1'')}-C_{(2'')}-C_{(3'')}$	119.4	121	120	120
$C_{(1'')}-C_{(6'')}-C_{(5'')}$	120.4	121	120	120
$C_{(2'')}-C_{(1'')}-C_{(6'')}$	119.5	118	120	120
$C_{(2'')}-C_{(3'')}-C_{(4'')}$	121.4	120	120	120
$C_{(3'')}-C_{(4'')}-C_{(5'')}$	119.3	120	120	120
$C_{(4'')}-C_{(5'')}-C_{(6'')}$	120.1	120	120	120
$C_{(1''')}-C_{(2''')}-C_{(3''')}$	120.3	120	120	120
$C_{(1''')}-C_{(6''')}-C_{(5''')}$	120.4	121	120	120
$C_{(2''')}-C_{(1''')}-C_{(6''')}$	118.6	118	119	119
$C_{(2''')}-C_{(3''')}-C_{(4''')}$	120.3	119	120	120
$C_{(3''')}-C_{(4''')}-C_{(5''')}$	120.3	119	120	120
$C_{(4''')}-C_{(5''')}-C_{(6''')}$	120.2	120	120	120
σ	0.5	2	2	4

TABLE 4. Endocylic Torsion Angles (τ) in the Tetracyclic System of the Molecule of Compound **3a** and Their Least Squares Deviation (σ, deg) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	τ, deg.			
	PCA	MNDO	AM1	PM3
$C_{(1)}-C_{(2)}-C_{(3)}-C_{(4)}$	-0.3	0	0	0
$C_{(2)}-C_{(3)}-C_{(4)}-C_{(4a)}$	-0.7	0	0	0
$C_{(3)}-C_{(4)}-C_{(4a)}-C_{(10a)}$	0.8	0	0	0
$C_{(4)}-C_{(4a)}-C_{(10a)}-C_{(1)}$	0.0	0	0	0
$C_{(4a)}-N_{(5)}-C_{(5a)}-N_{(10)}$	-26.9	-8	-7	-13
$C_{(4a)}-C_{(10a)}-C_{(1)}-C_{(2)}$	-0.9	0	0	0
$N_{(5)}-C_{(5a)}-N_{(10)}-C_{(10a)}$	26.2	8	7	13
$C_{(5a)}-C_{(6)}-C_{(7)}-C_{(8)}$	35.2	24	46	42
$C_{(5a)}-C_{(6)}-C_{(1')}-C_{(2')}$	51.6	46	53	56
$C_{(5a)}-N_{(10)}-C_{(10a)}-C_{(4a)}$	-16.7	-5	-5	-9
$C_{(6)}-C_{(7)}-C_{(8)}-C_{(9)}$	-4.1	-2	-21	-15
$C_{(6)}-C_{(1')}-C_{(2')}-C_{(3')}$	-51.4	-45	-53	-60
$C_{(7)}-C_{(8)}-C_{(9)}-N_{(10)}$	-6.4	-2	-4	-4
$C_{(8)}-C_{(9)}-N_{(10)}-C_{(5a)}$	-16.2	-19	1	-5
$C_{(9)}-N_{(10)}-C_{(5a)}-C_{(6)}$	47.6	41	26	33
$N_{(10)}-C_{(5a)}-C_{(6)}-C_{(7)}$	-56.9	-43	-49	-51
$N_{(10)}-C_{(10a)}-C_{(4a)}-N_{(5)}$	-1.2	-1	0	0
$C_{(10a)}-C_{(1)}-C_{(2)}-C_{(3)}$	1.0	0	0	0
$C_{(10a)}-C_{(4a)}-N_{(5)}-C_{(5a)}$	18.5	6	4	9
$C_{(1')}-C_{(2')}-C_{(3')}-C_{(4')}$	53.0	45	55	59
$C_{(2')}-C_{(3')}-C_{(4')}-C_{(5a)}$	-55.3	-48	-57	-55
$C_{(3')}-C_{(4')}-C_{(5a)}-C_{(6)}$	56.1	50	56	51
$C_{(4')}-C_{(5a)}-C_{(6)}-C_{(1')}$	-53.9	-48	-53	-51
σ	0.6	9	10	7

TABLE 5. Coordinates of Non-hydrogen Atoms (×10^4) in the Molecule of Compound **3a**

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
$C_{(1)}$	839(2)	6233(7)	8649(6)	$C_{(3')}$	1868(2)	3532(8)	3317(8)
$C_{(2)}$	452(2)	5366(8)	9243(7)	$C_{(4')}$	1907(2)	4545(7)	4707(7)
$C_{(3)}$	280(2)	3851(8)	8644(7)	$C_{(1'')}$	1767(2)	8607(7)	7852(6)
$C_{(4)}$	485(2)	3140(7)	7448(7)	$C_{(2'')}$	1733(2)	10420(7)	8047(7)
$C_{(4a)}$	866(2)	3950(7)	6868(6)	$C_{(3'')}$	1947(2)	11179(8)	9921(8)
$N_{(5)}$	1146(1)	3490(5)	5701(5)	$C_{(4'')}$	2185(2)	10214(9)	10192(8)
$C_{(5a)}$	1415(2)	5063(7)	5249(7)	$C_{(5'')}$	2213(2)	8396(8)	10010(7)
$C_{(6)}$	1138(2)	6098(6)	4147(6)	$C_{(6'')}$	2009(2)	7622(7)	8833(7)
$C_{(7)}$	1354(2)	7943(7)	3914(6)	$C_{(1''')}$	984(2)	9160(6)	3296(7)
$C_{(8)}$	1552(2)	8667(6)	5299(7)	$C_{(2''')}$	1002(2)	9661(7)	1873(7)
$C_{(9)}$	1568(2)	7822(6)	6522(7)	$C_{(3''')}$	658(2)	10746(8)	1317(7)
$N_{(10)}$	1438(1)	6014(5)	6621(5)	$C_{(4''')}$	293(2)	11308(8)	2154(8)
$C_{(10a)}$	1045(2)	5498(6)	7463(6)	$C_{(5''')}$	270(2)	10835(7)	3557(7)
$C_{(1')}$	1114(2)	5110(8)	2727(7)	$C_{(6''')}$	611(2)	9747(7)	4131(7)
$C_{(2')}$	1595(3)	4514(8)	2188(8)	—	—	—	—

TABLE 6. Bond Lengths (*d*) in the Molecule of Compound **11** and Their Least Squared Deviation (σ, Å) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	*d*, Å			
	PCA	MNDO	AM1	PM3
$C_{(1)}$–$C_{(2)}$	1.451	1.50	1.47	1.48
$C_{(1)}$–$C_{(10a)}$	1.356	1.36	1.35	1.34
$C_{(2)}$–$C_{(3)}$	1.475	1.51	1.48	1.49
$C_{(2)}$–O	1.237	1.23	1.24	1.22
$C_{(3)}$–$C_{(4)}$	1.331	1.35	1.34	1.34
$C_{(4)}$–$C_{(4a)}$	1.444	1.47	1.46	1.45
$N_{(5)}$–$C_{(4a)}$	1.285	1.30	1.30	1.30
$N_{(5)}$–$C_{(5a)}$	1.465	1.48	1.50	1.50
$C_{(6)}$–$C_{(5a)}$	1.549	1.58	1.56	1.55
$C_{(6)}$–$C_{(7)}$	1.553	1.57	1.53	1.54
$C_{(6)}$–$C_{(1')}$	1.535	1.55	1.52	1.53
$C_{(7)}$–$C_{(8)}$	1.510	1.51	1.49	1.49
$C_{(7)}$–$C_{(1''')}$	1.518	1.53	1.50	1.51
$C_{(8)}$–$C_{(9)}$	1.336	1.36	1.35	1.34
$C_{(9)}$–$N_{(10)}$	1.415	1.43	1.41	1.44
$C_{(9)}$–$C_{(1'')}$	1.490	1.49	1.48	1.47
$N_{(10)}$–$C_{(5a)}$	1.488	1.51	1.52	1.53
$N_{(10)}$–$C_{(10a)}$	1.367	1.41	1.41	1.43
$C_{(10a)}$–$C_{(4a)}$	1.472	1.50	1.51	1.48
$C_{(1')}$–$C_{(2')}$	1.531	1.54	1.51	1.52
$C_{(2')}$–$C_{(3')}$	1.519	1.54	1.51	1.52
$C_{(3')}$–$C_{(4')}$	1.526	1.54	1.51	1.52
$C_{(4')}$–$C_{(5a)}$	1.529	1.57	1.55	1.54
$C_{(1'')}$–$C_{(2'')}$	1.392	1.42	1.40	1.40
$C_{(1'')}$–$C_{(6'')}$	1.386	1.42	1.40	1.40
$C_{(2'')}$–$C_{(3'')}$	1.383	1.41	1.39	1.39
$C_{(3'')}$–$C_{(4'')}$	1.373	1.41	1.39	1.39
$C_{(4'')}$–$C_{(5'')}$	1.367	1.41	1.39	1.39
$C_{(5'')}$–$C_{(6'')}$	1.382	1.41	1.39	1.39
$C_{(1''')}$–$C_{(2''')}$	1.393	1.42	1.40	1.40
$C_{(1''')}$–$C_{(6''')}$	1.381	1.42	1.40	1.40
$C_{(2''')}$–$C_{(3''')}$	1.392	1.41	1.39	1.39
$C_{(3''')}$–$C_{(4''')}$	1.366	1.40	1.39	1.39
$C_{(4''')}$–$C_{(5''')}$	1.381	1.40	1.39	1.39
$C_{(5''')}$–$C_{(6''')}$	1.389	1.41	1.39	1.39
σ	0.005	0.03	0.02	0.02

In compound **3a** atom $N_{(10)}$ is 0.339 Å out of the $C_{(5a)}$, $C_{(9)}$, $C_{(10a)}$ plane, while in compound **11** it is only 0.159 Å out of the plane, i.e., the configuration of the bonds about $N_{(10)}$ in compound **11** is more planar than in **3a**. A more obvious way to estimate the extent of pyramidalization of the bonds may be to compare not the absolute values but the relative values calculated by the equation:

$$\xi = ((360 - \omega_\Sigma) / (360 - 320.1))\cdot 100\%$$

where ω_Σ is the sum of the bond angles at $N_{(10)}$, 320.1 is the sum of the bond angles at the nitrogen atom in the molecule of ammonia, and ξ is the relative degree of pyramidalization (with the pyramidalization of the bonds of the nitrogen atom in the molecule of ammonia taken as 100%). Evidently the value of ξ decreases from 40 to 10% in going from compound **3a** to **11**.

TABLE 7. Valence Angles (ω) in the Molecule of Compound **11** and Their Least Squares Deviation (σ, deg) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	ω, deg.			
	PCA	MNDO	AM1	PM3
$C_{(1)}-C_{(2)}-C_{(3)}$	118.8	118	117	118
$C_{(1)}-C_{(2)}-O$	121.8	122	122	121
$C_{(1)}-C_{(10a)}-C_{(4a)}$	122.1	122	122	122
$C_{(2)}-C_{(3)}-C_{(4)}$	123.4	123	123	123
$C_{(3)}-C_{(2)}-O$	119.4	121	121	121
$C_{(3)}-C_{(4)}-C_{(4a)}$	117.8	119	120	119
$C_{(4)}-C_{(4a)}-N_{(5)}$	126.1	128	130	128
$C_{(4a)}-N_{(5)}-C_{(5a)}$	107.6	110	108	110
$N_{(5)}-C_{(5a)}-C_{(4')}$	109.3	109	110	110
$C_{(5a)}-C_{(6)}-C_{(1')}$	109.9	111	110	110
$C_{(5a)}-C_{(4')}-C_{(3')}$	110.7	114	112	112
$C_{(6)}-C_{(5a)}-N_{(10)}$	108.7	113	112	112
$C_{(6)}-C_{(5a)}-N_{(5)}$	109.1	108	110	109
$C_{(6)}-C_{(5a)}-C_{(4')}$	112.3	113	110	113
$C_{(6)}-C_{(7)}-C_{(8)}$	113.2	114	112	113
$C_{(6)}-C_{(7)}-C_{(1''')}$	110.7	113	110	110
$C_{(6)}-C_{(1')}-C_{(2')}$	112.7	116	114	111
$C_{(7)}-C_{(6)}-C_{(5a)}$	110.2	113	111	111
$C_{(7)}-C_{(6)}-C_{(1')}$	112.3	114	112	110
$C_{(7)}-C_{(8)}-C_{(9)}$	125.1	127	124	124
$C_{(7)}-C_{(1''')}-C_{(2''')}$	119.7	120	120	120
$C_{(7)}-C_{(1''')}-C_{(6''')}$	121.1	122	121	121
$C_{(8)}-C_{(7)}-C_{(1''')}$	110.8	111	111	110
$C_{(8)}-C_{(9)}-N_{(10)}$	118.8	120	123	122
$C_{(8)}-C_{(9)}-C_{(1'')}$	123.6	122	119	121
$C_{(9)}-N_{(10)}-C_{(10a)}$	127.9	126	123	122
$C_{(9)}-N_{(10)}-C_{(5a)}$	119.0	119	118	118
$C_{(9)}-C_{(1'')}-C_{(2'')}$	119.3	121	119	120
$C_{(9)}-C_{(1'')}-C_{(6'')}$	121.7	121	121	120
$N_{(10)}-C_{(5a)}-N_{(5)}$	104.6	104	106	104
$N_{(10)}-C_{(5a)}-C_{(4')}$	112.5	109	109	109
$N_{(10)}-C_{(9)}-C_{(1'')}$	117.4	118	118	117
$N_{(10)}-C_{(10a)}-C_{(1)}$	133.8	134	132	131
$N_{(10)}-C_{(10a)}-C_{(4a)}$	104.0	105	106	106
$C_{(10a)}-C_{(1)}-C_{(2)}$	117.9	120	120	119
$C_{(10a)}-C_{(4a)}-C_{(4)}$	119.8	119	118	119
$C_{(10a)}-C_{(4a)}-N_{(5)}$	114.1	113	113	112
$C_{(10a)}-N_{(10)}-C_{(5a)}$	109.3	109	107	107
$C_{(1')}-C_{(2')}-C_{(3')}$	111.8	115	112	110
$C_{(2')}-C_{(3')}-C_{(4')}$	112.0	114	112	111
$C_{(1'')}-C_{(2'')}-C_{(3'')}$	120.3	121	120	120
$C_{(1'')}-C_{(6'')}-C_{(5'')}$	120.0	121	120	120
$C_{(2'')}-C_{(1'')}-C_{(6'')}$	118.9	119	120	120
$C_{(2'')}-C_{(3'')}-C_{(4'')}$	120.2	120	120	120
$C_{(3'')}-C_{(4'')}-C_{(5'')}$	119.8	120	120	120
$C_{(4'')}-C_{(5'')}-C_{(6'')}$	120.8	120	120	120
$C_{(1''')}-C_{(2''')}-C_{(3''')}$	119.8	121	120	120
$C_{(1''')}-C_{(6''')}-C_{(5''')}$	120.3	121	120	120
$C_{(2''')}-C_{(1''')}-C_{(6''')}$	119.2	117	119	120
$C_{(2''')}-C_{(3''')}-C_{(4''')}$	120.7	120	120	120
$C_{(3''')}-C_{(4''')}-C_{(5''')}$	119.7	119	120	120
$C_{(4''')}-C_{(5''')}-C_{(6''')}$	120.3	120	120	120
σ	0.3	2	2	2

TABLE 8. Endocylic Torsion Angles (τ) in the Tetracyclic System of the Molecule of Compound **11** and Their Least Squares Deviation (σ, deg) Determined by X-ray Crystallography (PCA), and MNDO, AM1, and PM3 Methods

Bond	τ, deg.			
	PCA	MNDO	AM1	PM3
$C_{(1)}-C_{(2)}-C_{(3)}-C_{(4)}$	3.1	0	0	1
$C_{(2)}-C_{(3)}-C_{(4)}-C_{(4a)}$	-1.1	1	0	0
$C_{(3)}-C_{(4)}-C_{(4a)}-C_{(10a)}$	-3.2	1	0	-1
$C_{(4)}-C_{(4a)}-C_{(10a)}-C_{(1)}$	5.4	-3	0	2
$C_{(4a)}-N_{(5)}-C_{(5a)}-N_{(10)}$	-3.6	-3	-4	-5
$C_{(4a)}-C_{(10a)}-C_{(1)}-C_{(2)}$	-3.1	4	0	0
$N_{(5)}-C_{(5a)}-N_{(10)}-C_{(10a)}$	6.6	3	6	8
$C_{(5a)}-C_{(6)}-C_{(7)}-C_{(8)}$	34.8	28	45	43
$C_{(5a)}-C_{(6)}-C_{(1')}-C_{(2')}$	53.1	47	54	56
$C_{(5a)}-N_{(10)}-C_{(10a)}-C_{(4a)}$	-6.7	-2	-6	-8
$C_{(6)}-C_{(7)}-C_{(8)}-C_{(9)}$	-4.9	-5	-20	-17
$C_{(6)}-C_{(1')}-C_{(2')}-C_{(3')}$	-53.7	-45	-54	-61
$C_{(7)}-C_{(8)}-C_{(9)}-N_{(10)}$	-4.2	-2	-3	-4
$C_{(8)}-C_{(9)}-N_{(10)}-C_{(5a)}$	-19.9	-17	-3	-5
$C_{(9)}-N_{(10)}-C_{(5a)}-C_{(6)}$	50.0	40	30	33
$N_{(10)}-C_{(5a)}-C_{(6)}-C_{(7)}$	-55.3	-44	-50	-51
$N_{(10)}-C_{(10a)}-C_{(4a)}-N_{(5)}$	4.7	1	4	5
$C_{(10a)}-C_{(1)}-C_{(2)}-C_{(3)}$	-1.0	-2	0	-1
$C_{(10a)}-C_{(4a)}-N_{(5)}-C_{(5a)}$	-0.5	1	0	0
$C_{(1')}-C_{(2')}-C_{(3')}-C_{(4')}$	54.2	45	54	59
$C_{(2')}-C_{(3')}-C_{(4')}-C_{(5a)}$	-55.3	-48	-57	-54
$C_{(3')}-C_{(4')}-C_{(5a)}-C_{(6)}$	55.9	50	56	50
$C_{(4')}-C_{(5a)}-C_{(6)}-C_{(1')}$	-54.5	-49	-54	-51
σ	0.3	6	7	6

TABLE 9. Coordinates on Non-hydrogen Atoms (× 10^4) in the Molecule of Compound **11**

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
$C_{(1)}$	1385(4)	-1247(2)	7084(2)	$C_{(3')}$	-1383(4)	1663(2)	7861(2)
$C_{(2)}$	312(4)	-1772(2)	6594(2)	$C_{(4')}$	-251(4)	1042(2)	8175(2)
$C_{(3)}$	-1372(4)	-1556(2)	6223(2)	$C_{(1'')}$	3992(4)	-355(2)	8518(2)
$C_{(4)}$	-1941(4)	-894(2)	6276(2)	$C_{(2'')}$	5676(4)	-472(2)	8429(2)
$C_{(4a)}$	-852(4)	-365(2)	6732(2)	$C_{(3'')}$	6540(4)	-952(2)	9027(2)
$N_{(5)}$	-1155(3)	303(1)	6792(2)	$C_{(4'')}$	5744(5)	-1318(2)	9712(2)
$C_{(5a)}$	297(4)	637(2)	7298(2)	$C_{(5'')}$	4087(5)	-1205(2)	9804(2)
$C_{(6)}$	1155(4)	1127(2)	6588(2)	$C_{(6'')}$	3201(4)	-727(2)	9213(2)
$C_{(7)}$	2877(4)	1370(2)	7041(2)	$C_{(1''')}$	3973(4)	1622(2)	6266(2)
$C_{(8)}$	3748(4)	809(2)	7667(2)	$C_{(2''')}$	4069(4)	2343(2)	6055(2)
$C_{(9)}$	3098(4)	182(2)	7888(2)	$C_{(3''')}$	5032(5)	2574(2)	5326(2)
$N_{(10)}$	1428(3)	35(2)	7570(2)	$C_{(4''')}$	5893(4)	2099(2)	4810(2)
$C_{(10a)}$	792(4)	-577(2)	7164(2)	$C_{(5''')}$	5816(4)	1381(2)	5021(2)
$C_{(1')}$	18(4)	1757(2)	6298(2)	$C_{(6''')}$	4865(4)	1144(2)	5752(2)
$C_{(2')}$	-574(4)	2158(2)	7169(2)	O	773(3)	-2391(2)	6477(2)

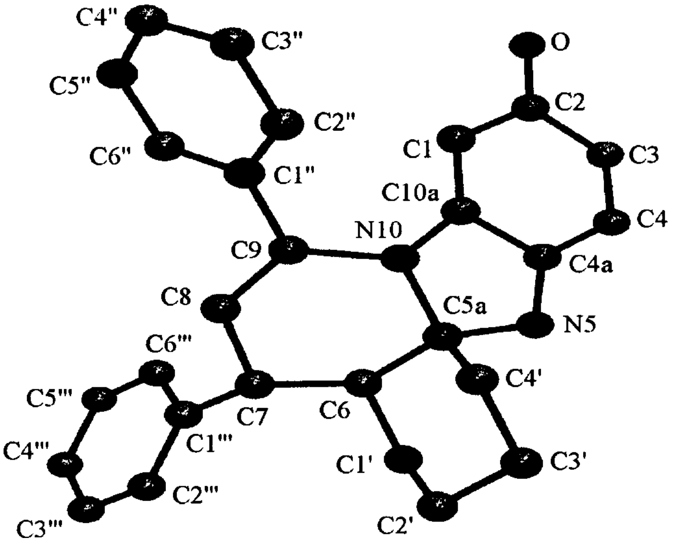

Fig. 1. General view of the molecule of compound **11**.

Ring D in both compounds has the chair form in both compounds. The A/B fusion is quasi-*cis*, B/C is planar, and A/D is *cis* which confirms previous suggestions. The planes of the aromatic rings E and F are rotated relative to the compressed part of ring A. Comparison of the values of the torsion angles $C_{(6)}–C_{(7)}–C_{(1''')}–C_{(2''')}$ (106° and 96°), $C_{(8)}–C_{(7)}–C_{(1''')}–C_{(6''')}$ (51° and 44°), $C_{(8)}–C_{(9)}–C_{(1'')}–C_{(2')}$ (-30° and -40°), and $N_{(10)}–C_{(9)}–C_{(1'')}–C_{(6'')}$ (-29° and -38°) in compounds **3a** and **11** respectively shows that in the latter, along with the compression of ring B and the introduction of an oxygen atom at position 2, the angle of rotation of ring E is increased by about 10°, and that of ring F is decreased by approximately the same amount.

For compound **3a** the distance (r) from atom $H_{(1)}$ to the center of the screening ring E is 3.26 Å and the angle (Ψ) between the plane of ring E and the line joining $H_{(1)}$ to the center of the ring is 54°; for compound **11** these values are 3.14 Å and 58° respectively. From these values the contribution of ring E to the screening of the proton $H_{(1)}$ in compound **3a** is 0.8 ppm, according to [5], and for compound **11** is 1.05 ppm (signal shifts to high field). Comparison of the values of the chemical shifts for the $H_{(1)}$ protons for the given compounds with those for compounds **9b** and **14b**, which do not have screening benzene rings (Table 1), gives a high field shift for compound **3a** in comparison with **9b** of 1.0 ppm, and for compound **11** in comparison with **14b** of 1.07 ppm, which agrees satisfactorily with the calculated values.

We propose that the other compounds discussed (at the least those with a notable shift to high field of proton $H_{(1)}$, i.e., compounds **1-8**, **10**, **12**, **13**) have analogous spatial configurations. To confirm this proposal (taking into account the opposite nature of the reaction leading to the synthesis of 5,5a,6,7-tetrahydropyrido-[1,2-*a*]benzimidazoles and 6,7-dihydro-5aH-pyrido[1,2-*b*]benzoxazoles), we calculated the Gibbs free energy of formation (ΔG_f) of compounds **3a** and **5** with the two configurations of *cis* and *trans* fusion of rings A and D using a complex of semiempirical methods (MNDO, AM1, PM3) (Table 10). The ground state analysis of compound **3a** showed that the greatest contribution to the lowering of its energy came from an increase in the electron-nuclear attraction, i.e., the bond energy. Analysis of this in terms of the localized molecular orbital formalism shows that, in the configuration with *cis* fusion of rings A and D, the sum of the n-π^* interactions is large and there is delocalisation of the unshared electron pair of atom $N_{(10)}$ with the aromatic ring to which it is bonded. On going from *cis* to *trans* fusion of rings A and D the extent of pyramidalization of $N_{(10)}$ is increased by a factor close to two (Table 10). Hence there is excellent agreement between the experimentally determined

TABLE 10. Gibbs Free Energies of Formation (ΔG_f, kJ/mol) and Relative Energies ($\Delta\Delta G_f$, kJ/mol) for the Configurations of Compounds **3a** and **5**; and Degree of Pyramidalization of the Bonds at $N_{(10)}$ (ξ, %) Determined by MNDO, AM1, and PM3 Methods and X-ray Crystallography

Compound	Method	*cis* fusion of A and D		*trans* fusion of A and D		$\Delta\Delta G_f$
		ΔG_f	ξ	ΔG_f	ξ	
3a	MNDO	258.8	14	274.2	52	-15.4
	AM1	287.6	36	296.2	68	-8.6
	PM3	166.4	36	188.1	62	-21.7
	PCA	—	40	—	—	—
5	MNDO	231.9	18	250.9	51	-19.0
	AM1	260.9	33	262.8	68	-1.9
	PM3	135.6	37	148.3	62	-12.7

geometric parameters with the semiempirical methods for compounds **3a** and **11** (Tables 2-4, 6-8). The MNDO method gave the smallest error (Table 10) in determining the distance between atom $H_{(1)}$ and the center of ring E which is explained by the excellent derivation of the torsion angles $C_{(6)}$–$C_{(7)}$–$C_{(8)}$–$C_{(9)}$ and $C_{(8)}$–$C_{(9)}$–$N_{(10)}$–$C_{(5a)}$.

Comparison of the values of the chemical shifts of proton $H_{(1)}$ for the different compounds (see Table 1) permits a number of points to be made.

1. In most cases of the derivatives of 6,7-dihydro-5aH-pyrido[1,2-*b*]benzoxazole the signal is found at 0.05-0.15 ppm to weak field relative to the corresponding derivatives of 5,5a,6,7-tetrahydropyrido[1,2-*a*]-benzimidazole (with the exception of the identical chemical shifts for compounds **1a** and **2**); calculations show (Table 11) that in going from compound **5** to **6b** the distance between atom $H_{(1)}$ and the center of the screening ring E is increased.

2. In 7-phenyl substituted derivatives of 5,5a,6,7-tetrahydropyrido[1,2-*a*]benzimidazole and 6,7-dihydro-5aH-pyrido[1,2-*b*]benzoxazole the signal appears at 0.05-0.15 ppm to weaker field than in the corresponding compounds without a substituent at position 7 (**1a,b, 6a,b, 10a,b 14a,b**). Calculations for compounds **6a** and **6b** show that this is caused by an increase in the distance between $H_{(1)}$ and the screening ring E which, in its turn, is connected with small decrease in the angle $C_{(1)}$–$C_{(10a)}$–$N_{(10)}$–$C_{(9)}$ when a bulky substituent is introduced.

3. Replacement of the 5a,6-tetramethylene unit by a 5a-phenyl leads to a shift of the signal to weak field (by 0.26 ppm on going from compound **3a** to **1b**, and by 0.18 ppm on going from compound **11** to **10b**). The reason is also probably deformation of ring A.

TABLE 11. Distance (r, Å) from Atom $H_{(1)}$ to the Center of the Screening Ring E and the Angle (Ψ, deg) Between the Plane of Ring E and the Line from $H_{(1)}$ to the Center of Ring E Obtained by X-ray Crystallography (PCA) and MNDO, AM1, and PM3 methods for Compounds **3a**, **5**, **6a**,**b**, and **11**

Compound	PCA		MNDO		AM1		PM3	
	r	Ψ	r	Ψ	r	Ψ	r	Ψ
3a	3.26	53.9	3.10	63	2.75	64	2.79	63
5	—	—	3.48	56	3.03	60	3.10	59
6a	—	—	3.41	58	3.04	61	3.09	61
6b	—	—	3.52	58	3.08	61	3.14	61
11	3.14	57.6	3.11	62	282	64	2.82	64

4. Introduction of either electron donor or acceptor substituents in the *para* position of the screening ring has practically no effect on the chemical shift of the $H_{(1)}$ proton signal (compounds **3b,c**). In contrast, introduction of a substituent in the *ortho* position (compound **3d**) caused a shift of the signal by about 0.3 ppm evidently because the presence of the *ortho* substituent increases the angle of rotation of the screening ring relative to the distorted part of ring A, and consequently the angle Ψ is increased.

5. In compounds **5-8**, **12**, and **13**, in which the screening ring E is bonded to ring A *via* the $–CH_2–CH_2–$ group, the signal is significantly shifted to weak field in comparison with compounds **3** and **11**. Calculations showed that in compound **5,** in comparison with compound **3a**, the angle of rotation of the screening ring E relative to ring A is decreased which leads to an increase in the distance between its center and $H_{(1)}$ and a small decrease in the angle Ψ.

EXPERIMENTAL

^1H NMR spectra were recorded in deuterochloroform with TMS as internal standard on Bruker HE-90X and WM-250 instruments. X-ray crystallographic studies were carried out with a Hilger-Watts 4-circle automatic diffractometer ($\lambda MoK\alpha$, graphite monochromator, $2\theta/\omega$ scanning).

Rhombic monocrystals of compound **3a** ($C_{27}H_{26}N_2$) were grown from a solution in 4:1 ethanol–DMF. Space group $Pca2_1$; $Z = 4$; $a = 28.308(2)$, $b = 7.700(1)$, $c = 9.399(1)$ Å; $V = 2048.7$ Å^3; M = 378, $\rho_{calc} = 1.23$ g/cm^3, $\mu = 0.78$ cm^{-1}. The intensities of 972 independent reflexions were measured in the range with maximum value of $\sin(\theta/\lambda) = 6.76$ nm^{-1}. Lorentz and polarization corrections were introduced in converting intensities to structure factors. The structure was solved by direct methods and refined by least squares in the anisotropic approximation to $R = 0.04$ (972 reflexions). Positions of hydrogen atoms were determined geometrically.

Monoclinic monocrystals of compound **11** ($C_{27}H_{24}N_2O$) were grown from a solution in 1:3 benzene–hexane. Space group $P2_1/n$; $Z = 4$; $a = 8.072(1)$, $b = 18.812(2)$, $c = 13.902(1)$ Å; $\beta = 94.07°$; $V = 2105.8$ Å^3; M = 392, $\rho_{calc} = 1.24$ g/cm^3, $\mu = 0.82$ cm^{-1}. Intensities of 2372 observed reflexions with $I > 1.96\sigma(I)$ were measured in the range of 2θ up to 60°. The structure was solved by direct methods and refined by least squares in the anisotropic approximation to $R = 0.05$ (2372 reflexions). All calculations were carried out with the INEXTL program [7].

Semiempirical calculations were carried out using the MOPAC 6.0 package of programs for the gas phase with complete optimization of the geometry and the use of RHF formalism.

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