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Study on the Atropisomerism of Some New 2-Aryl-1,3-Dioxanes

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Abstract: The synthesis and the stereochemistry of a new class of compounds showing atropisomerism, the 1,3-dioxane derivatives bearing disymmetric axial aryl groups in position 2 of the 1,3-dioxane ring are reported.

INTRODUCTION

Studies[1-4] on the stereochemistry of 2-methyl-2-aryl-1,3-dioxanes showed the high preference of the aromatic group for axial orientation, the conformational equilibrium A $\rightleftharpoons$ B (Scheme 1) being strongly shifted towards conformation A. The investigations on this equilibrium in the case of 2-methyl-2-phenyl-1,3-dioxane revealed the considerably higher preference of the phenyl group for the axial orientation ($\Delta G^\circ = 2.42$ kcal/mol)[1] as it was expected considering the A-values (conformational free energies) of the two substituents located in position 2 of the heterocycle ($\Delta G^\circ_{Me}-\Delta G^\circ_{Ph} = 0.8$ kcal/mol).[1]

On the other side the studies[1,3-8] on the rotameric behaviour of the axial phenyl group located in position 2 of the 1,3-dioxane ring pointed out the higher preference of this substituent for the orthogonal

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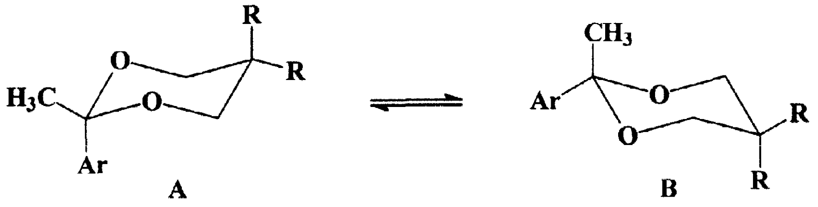
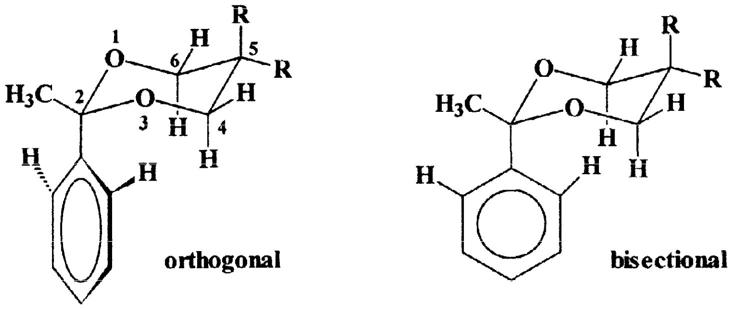
conformer than for the bisectional disposition (Scheme 2), in agreement with smaller interactions in this rotamer between the aromatic ring and the axial protons in positions 4 and 6.



Scheme 1

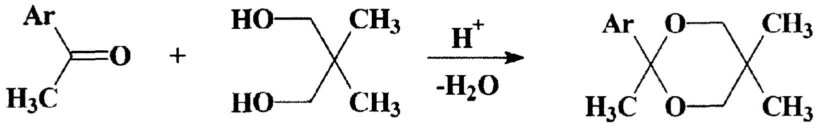


Scheme 2

The investigations on the stereochemistry of some new 1,3-dioxane derivatives bearing disymmetric axial aryl groups in position 2 of the heterocycle should reveal interesting aspects. The steric hindrance of the rotation of the aryl group around its bond with the 1,3-dioxane ring should determine the axial chirality of the compounds. The chirality of the molecules can be observed in NMR spectra by the diastereotopicity of positions 4 and 6 of the 1,3-dioxane ring.

RESULTS AND DISCUSSION

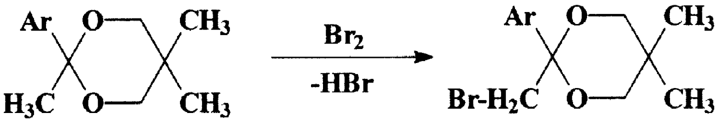
New 2-aryl-1,3-dioxanes (**1-4**) have been obtained by the reaction of some methyl, aryl ketones with 2,2-dimethyl-1,3-propanediol (Scheme 3).



Ar = o-C_6H_4-NO_2	**1**
Ar = m-C_6H_4-NO_2	**2**
Ar = α-$C_{10}H_7$	**3**
Ar = β-$C_{10}H_7$	**4**

Scheme 3

The previously synthesised 1,3-dioxanes (**1-4**) were reacted with bromine to give the new brominated compounds **5-8** (Scheme 4).



Ar = o-C_6H_4-NO_2 **5**
Ar = m-C_6H_4-NO_2 **6**
Ar = α-$C_{10}H_7$ **7**
Ar = β-$C_{10}H_7$ **8**

Scheme 4

All the investigated compounds exhibit anancomeric structures, the conformational equilibrium A $\rightleftharpoons$ B being shifted towards the conformer that displays the aromatic substituent in axial orientation (A, Scheme 1).

The "rigid" structures of the compounds determine the recording in the NMR spectra of different signals for the equatorial and axial protons of the 1,3-dioxane ring (positions 4 and 6) and for the protons and carbon atoms belonging to the axial and equatorial methyl groups in position 5 (Table 1). The differences between the chemical shifts of the protons of the heterocycle ($\Delta\delta_{4(6)ax-4(6)eq}$ = 0.02-0.16) are considerably smaller than usual ($\Delta\delta_{4(6)eq-4(6)ax}$ = 0.4-0.8)[1,3,9-11] and even more the axial protons become in the majority of cases more deshielded than the equatorial ones. This unusual situation is due in one side to the deshielding of the axial protons in positions 4 and 6 by the "steric compression" exerted by the axial aromatic group on these protons (i.e. similar influences have been observed for axial alkyl groups in 2,2-disubstituted-1,3-dioxane derivatives)[12-15] and on another side to the influence through space of the anysotropic magnetic field of the axial aromatic group that prefers the orthogonal disposition. The equatorial protons in positions 4 and 6 are located in the shielding area of the magnetic field generated by the axial aromatic group while the axial protons of same positions are disposed in the region of deshielding of the mentioned magnetic field. A very strong influence of the magnetic field of the aromatic substituents has been observed on the protons of the equatorial methyl group in position 5. The signals of these protons are strongly shielded, their chemical shifts being close of that of TMS and in the case of compound **5** even a negative value of the chemical shift for these protons has been recorded [$\delta_{5\text{-}Me(eq)} = -0.01$].

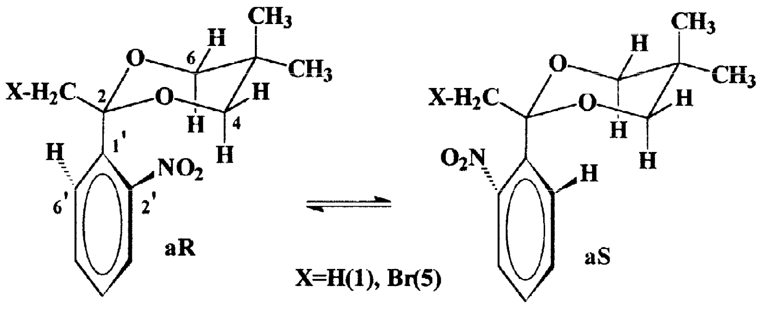
The assignment of the signals belonging to the protons of the heterocycle has been performed taking into account the results of NOE experiments. These experiments confirmed also the axial orientation of the aromatic groups. The irradiation of the signal due to the protons of the methyl or bromomethyl group in position 2, if these substituents show equatorial position, should exhibit in the NOEDiff. spectrum a weak influence only on the signal belonging to the equatorial protons in position 4 and 6. If the irradiated group shows axial orientation, the NOEDiff. spectrum should show an influence on both signals (due to the axial and equatorial protons) with a higher intensity on the signal due to the axial protons. In all the investigated compounds only a weak influence on one of the doublets belonging to the characteristic AB system has been observed, confirming the axial orientation of the aromatic group and making possible the assignment of the signals belonging to the equatorial protons.

Table 1. NMR data (δ, ppm) for compounds **1-8** (spectra run at room temperature).

Com pound	^{1}H						^{13}C	
	4,6-H$_{eq}$	4,6-H$_{ax}$	Δ	5-CH$_3$(ax)	5-CH$_3$(eq)	2-CH$_2$-Br	5-CH$_3$(ax)	5-CH$_3$(eq)
1	3.17	3.21	0.04	1.08	0.10	-	22.15	21.31
2	3.14	3.05	0.09	1.11	0.17	-	22.38	21.29
3	3.25	3.39	0.14	1.26	0.10	-	22.89	21.28
4	3.35	3.49	0.14	1.25	0.23	-	22.79	21.35
5	3.05	3.17	0.12	1.12	-0.01	3.81	22.21	20.81
6	2.96	3.12	0.16	1.15	0.09	3.13	22.36	21.04
7	3.25, 3.27*		0.02	1.38	0.02	3.60	23.28	21.38
8	3.31	3.36	0.05	1.34	0.10	3.45	22.78	21.09

*The assignment for the axial and equatorial positions is not possible in this case

In the orthogonal rotamer the disymmetry of the aromatic group introduces the axial chirality of the molecules. The rotation of the aryl group (free at room temperature) around its bond with the 1,3-dioxane ring results into an enantiomeric inversion. As an example, in the cases of compounds **1** and **5** (Scheme 5) the axis C^2-$C^{1'}$ is a chiral element and the reference groups are H (6') and NO_2 (2') at one extremity of the axis and CH_2-X and the 1,3-dioxane ring at the other extremity of the chiral axis.



Scheme 5

The other investigated compounds exhibit also axial chirality, the bond of the aromatic group with the 1,3-dioxane ring being a chiral axis. The reference groups are H (5') and NO_2 (3') for compounds **2** and **6**, H (2') and $C^{8'}$ for compounds **3** and **7** and H (3') and $C^{8'}$ in the case of compounds **4** and **8**.

The chirality of the molecule introduces the diastereotopicity of positions 4 and 6 of the 1,3-dioxane ring (compounds **1-8**) and of the heterotopic protons of the bromomethyl group in 2 (compounds **5-8**).

The possible hindrance of the rotation of the aryl groups around their bonds with the heterocycle should generate the atropisomery of these compounds. For solving the problem of the stability of the atropisomers variable temperature NMR investigations have been performed.

At room temperature, the rotation of the aromatic substituent around its bond with the heterocycle is fast and in the NMR time scale the positions 4 and 6, as well as the heterotopic protons of the bromomethyl group are render equivalent, unique signals being recorded (Table 1).

The low temperature NMR experiments (compounds **1-6**) showed the freezing of the rotation of the aromatic groups in the range of temperatures -10 °C - -40 °C. The spectra recorded at low temperature exhibit different signals for the protons of positions 4 and 6, render diastereotopic in the chiral frozen structure of the compounds (Table 2). The diastereotopicity of the axial protons are considerably higher than that determined for the equatorial ones.

The ^{1}H NMR spectra [D$_8$]-toluene of compounds **3** (Fig. 1a) and **4** (Fig. 2a) run at room temperature exhibits for the protons of the 1,3-dioxane ring (positions 4 and 6) two doublets (AB system) the more deshielded belonging to the axial protons (compound **3**: $\delta_{4(6)eq} = 3.26$ and $\delta_{4(6)ax} = 3.41$; compound **4**: $\delta_{4(6)eq} = 3.33$ and $\delta_{4(6)ax} = 3.47$). The variable temperature experiment of compound **3** showed at - 20 °C (Fig. 1b) the coalescence of the signals due to the axial protons, at -30 °C (Fig. 1c) the coalescence of the signals belonging to the equatorial protons while at - 60 °C the ^{1}H NMR spectrum (Fig. 1d) shows well separated signals for the protons of positions 4 and 6 ($\delta_{4ax} = 3.21$, $\delta_{4eq} = 3.14$; $\delta_{6ax} = 3.82$, $\delta_{6eq} = 3.41$). The NMR differentiation of positions 4 and 6 is due to the chirality of the molecule displaying the frozen orthogonal rotamer of the aryl group. The variable temperature experiment of compound **4** showed the coalescence of the signals due to the axial protons at - 30 °C (Fig. 2b) and at - 50 °C (Fig. 2c) well separated signals for the protons of positions **4** and 6 [$\delta_{4ax} = 3.38$, $\delta_{6ax} = 3.56$ and $\delta_{4(6)eq} = 3.29$] have been obtained. The stronger influence of the disymmetry of the frozen orthogonal conformer of the aryl group on the axial protons results in the closer position of these protons to the axial disymmetric aromatic substituent.

Table 2. ^{1}H NMR data (δ, ppm) of compounds **1-6** in low temperature spectra. [a]

Compound	T(K)	Positions 4 and 6						-CH(H')Br
		4-ax	6-ax	$\Delta_{6ax-4ax}$	4-eq	6-eq	$\Delta_{6ax-4ax}$	
1	233	3.02	3.18	0.16	3.02	3.18	0.16	-
2	223	3.00	3.08	0.08	2.93	2.93	-	-
3	213	3.21	3.82	0.61	3.14	3.41	0.27	-
4	223	3.38	3.56	0.18	3.29	3.29	-	-
5	213	3.20	3.31	0.11	3.06	3.23	0.17	3.42, 4.21
6	203	3.04	3.18	0.14	2.94	2.94	-	[b]

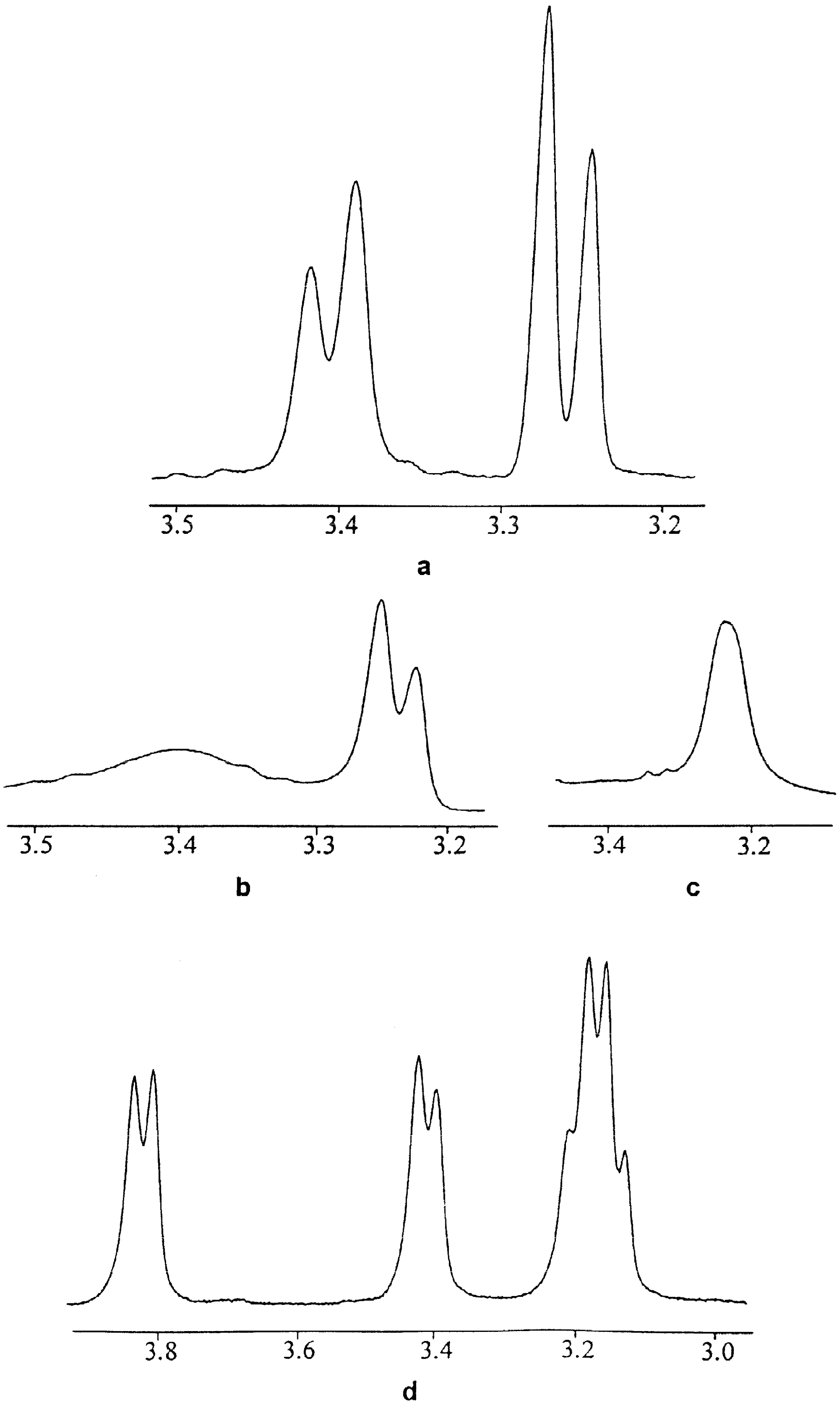


Fig. 1. ^{1}**H NMR spectra of compound 3**: at room temperature (a), at –20°C (b), at –30°C (c) and at –60°C (d).

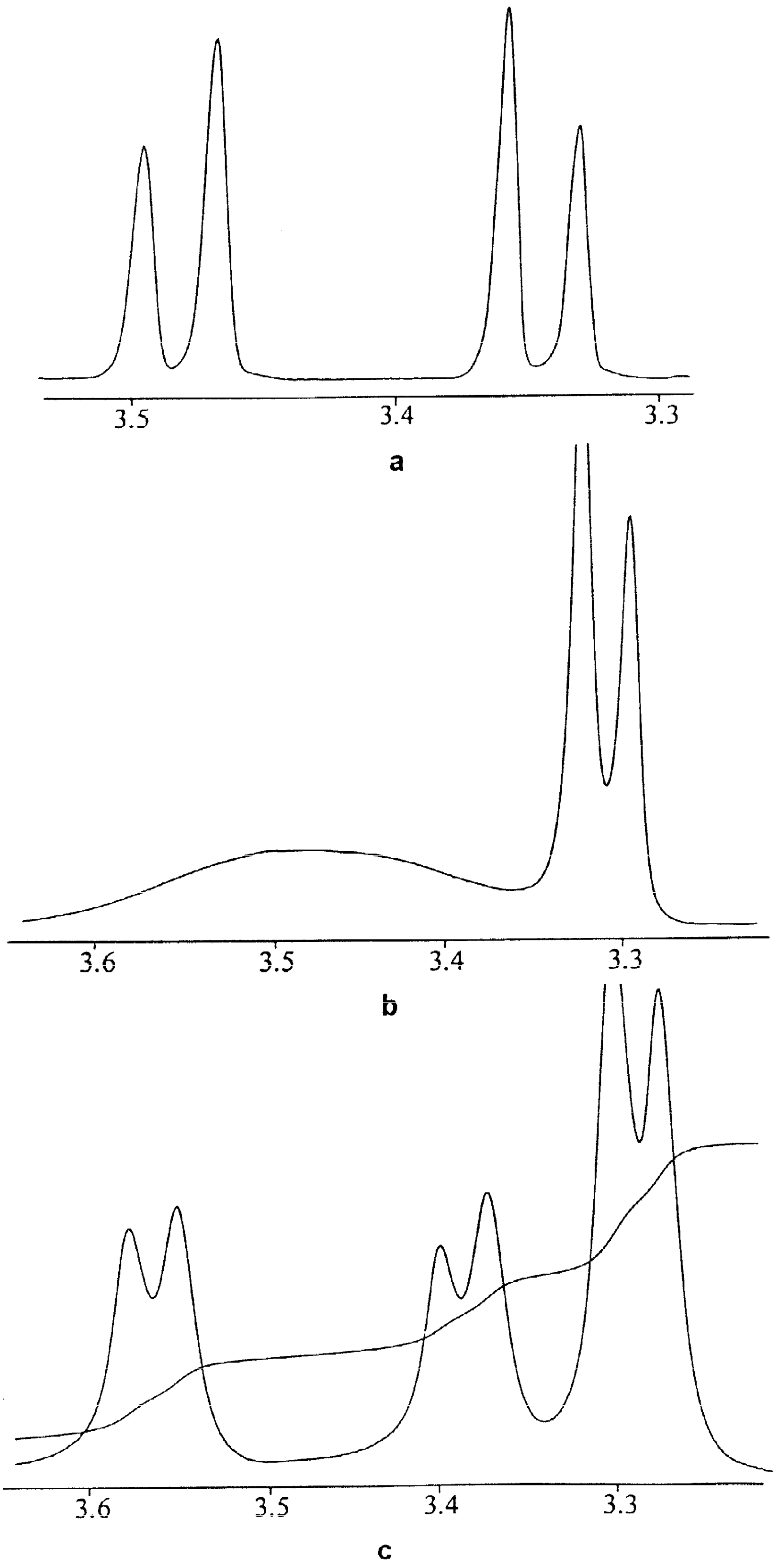


Fig. 2. ^{1}H NMR spectra of compound **4**: at room temperature (a), at - 30 °C (b) and at - 50 °C (c).

The variable temperature NMR experiment [D$_8$]-toluene run with compound **5** showed the transformation of the room temperature recorded AB system ($\delta_{4(6)ax}$ = 3.28 and $\delta_{4(6)eq}$ = 3.19; Fig. 3a) belonging to the protons of the heterocycle into two AB systems (δ_{4ax} = 3.20, δ_{4eq} = 3.06, δ_{6ax} = 3.31 and δ_{6eq} = 3.23) observed in the low temperature spectrum (- 60 °C, Fig. 3b).

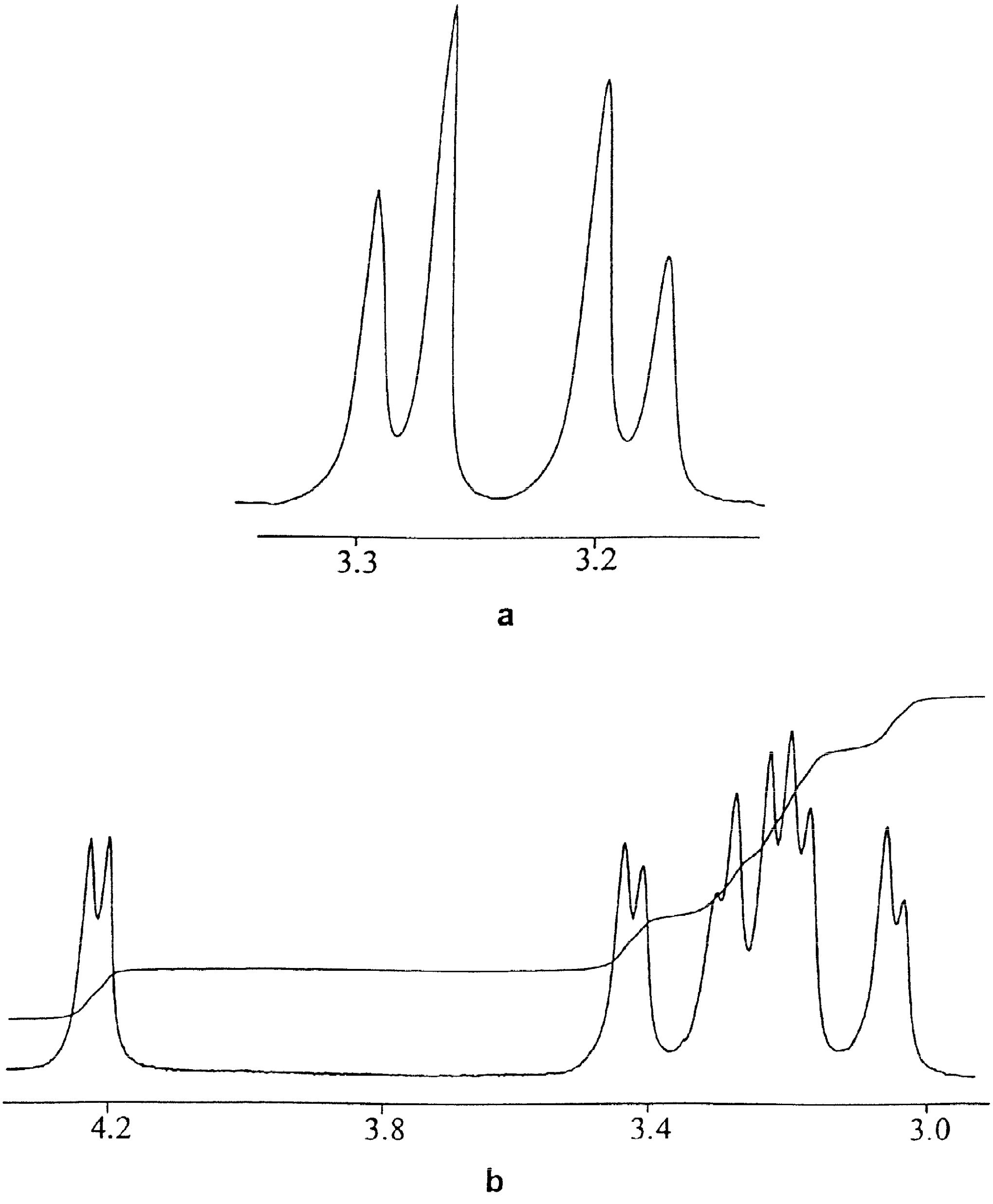


Fig. 3. ^{1}H NMR spectra of compound 5: at room temperature (a) and at - 60 °C (b).

Spectacular changes have been recorded for the signal due to the heterotopic protons of the bromomethyl group. If at room temperature the rotation of the aryl group renders equivalent these protons from the NMR point of view (singlet $\delta = 3.80$) in the frozen structure the signals of these protons (two doublets, $\delta = 4.21$, $\delta' = 3.44$, $J = 10.7$ Hz) exhibit a very high diastereotopicity ($\Delta\delta = 0.77$).

CONCLUSIONS

The study on the stereochemistry of 1,3-dioxane derivatives bearing disymmetric aryl groups in position 2 of the heterocycle shows the higher preference of these aromatic substituents for the axial orientation than that of the methyl or bromomethyl groups. The preference of the aryl groups for orthogonal rotamers results into significant modifications of the chemical shifts of the signals belonging to the protons of the heterocycle and of the equatorial methyl group in position 5. The hindrance of the rotation of the aryl group around its bond with the 1,3-dioxane ring introduces the axial chirality of the molecules observed (in low temperature spectra) by the diastereotopicity of the protons located in 4 and 6 or in the bromomethyl substituent. The configurational isomers vis à vis of this chiral axis represent a new class of atropisomers.

EXPERIMENTAL

^{1}H-and ^{13}C-NMR spectra were recorded at room temperature, using C_6D_6 as solvent, in 5 mm tubes, on a Bruker AM 400 Fourier transform NMR spectrometer, equipped with a dual ^{13}C-^{1}H head, operating at 400 MHz for protons and 100 MHz for carbon atoms.

M.ps were measured with Electrothermal melting point apparatus and are uncorrected.

Compounds 1-4, general procedure. - Stoichiometric amounts of 1,3-diol (0.2 mol) and ketone (0.1 mol) with catalytic amounts of p-toluenesulphonic acid (0.1 g) were dissolved in 200 ml benzene. The mixture was refluxed and the water resulted in the reaction was removed using a Dean-Stark trap. When 80 % of the theoretical water was separated, after cooling at room temperature, the catalyst was neutralised (under stirring 0.5 h) with CH_3-COONa powder in excess (0.2 g). The reaction mixture was washed twice with 100 ml water. After drying (with Na_2SO_4) the benzene was removed and the 1,3-dioxane compounds were purified by crystallisation from ethanol or by vacuum distillation.

Compounds 5-8, general procedure. - 0.1 mol 1,3-dioxane compound and 100 ml dry diethyl ether (or dichlorometane) were introduced in a four necked flask equipped with a reflux condenser, a mechanic stirring system, a thermometer and a dropping funnel. To this mixture cooled in an ice bath at 0-5° C, the corresponding (0.1 mol) amount of bromine was added dropwise, under stirring, monitoring at the beginning the fading of the solution colour. When the addition of the bromine was finished the ice bath was removed and the stirring was continued for an hour. The temperature in the flask reached slowly the room value (20-25°C).

The organic solvent and the resulted HBr were removed in vacuum. The products were purified by crystallisation from ethanol or a mixture of ethanol and chloroform.

2,5,5-Trimethyl-2-*ortho*-nitrophenyl-1,3-dioxane 1. White crystals, m.p. 103-104 °C, 7.13 g (0.0305 mol) yield 61 %. Found: C, 62.25; H, 6.97; N, 5.42. $C_{13}H_{17}NO_4$ requires C, 62.14; H, 6.82; N, 5.57. δ_H (C_6D_6) 0.10 [3H, s, 5-CH_3(eq)], 1.08 [3H, s, 5-CH_3(ax)], 1.91[3H, s, 2-CH_3(eq)], 3.17 (2H, d, J = 10.8 Hz, H_{eq}-4, H_{eq}-6), 3.21 (2H, d, J = 10.8 Hz, H_{ax}-4, H_{ax}-6), 6.71 (1H, ddd, $J \approx J' \approx 8.0$, J'' = 1.2 Hz, H-5'), 6.87 (1H, dd, J = 8.0, J' = 1.0 Hz, H-6'), 6.92 (1H, ddd, $J \approx J' \approx 8.0$, J'' = 1.0 Hz, H-4'), 7.36 (1H, dd, J = 8.0, J' = 1.2 Hz, H-3'). δ_C (C_6D_6) 21.01 [Me(eq)-5], 22.15 [Me(ax)-5], 29.15 (C-5), 30.66 [Me(eq)-2], 71.98 (C-4, C-6), 99.05 (C-2), 123.08, 128.89, 129.16, 130.24 (tertiary aromatic carbon atoms), 132.68 (C-1'), 150.42 (C-2').

2,5,5-Trimethyl-2-*metha*-nitrophenyl-1,3-dioxane 2. White crystals, m.p. 92-93 °C, 7.60 g (0.033 mol) yield 65 %. Found: C, 61.97; H, 6.94; N, 5.74. $C_{13}H_{17}NO_4$ requires C, 62.14; H, 6.82; N, 5.57. δ_H (C_6D_6) 0.17 [3H, s, 5-CH_3(eq)], 1.11 [3H, s, 5-CH_3(ax)], 1.46 [3H, s, 2-CH_3(eq)], 3.05 (2H, d, J = 10.9 Hz, H_{eq}-4, H_{eq}-6), 3.14 (2H, d, J = 10.9 Hz, H_{ax}-4, H_{ax}-6), 6.80 [1H, t(overlapped dd), $J \approx J' \approx 7.8$ Hz, H-6'), 7.40 [1H, dt (overlapped ddd, $J \approx J' \approx 7.8$, " = 2.0 Hz, H-5'), 7.78 (1H, ddd, $J \approx J' \approx 7.8$, J'' = 2.0 Hz, H-4'), 8.38 [1H, t (overlapped dd), $J \approx J' \approx 2.0$ Hz, H-2']. δ_C (C_6D_6) 21.29 [Me(eq)-5], 22.38 [Me(ax)-5], 29.47 (C-5), 31.24 [Me(eq)-2], 71.34 (C-4, C-6), 99.22 (C-2), 121.60, 122.50, 129.42, 132.40 (tertiary aromatic carbon atoms), 143.94 (C-1'), 148.98 (C-2').

2,5,5-Trimethyl-2-α-naphtyl-1,3-dioxane 3. Colorless liquid, b.p. 125-127 °C (1 mm colHg), 6.65 g (0.026 mol) yield 52 %. Found: C, 79.74; H, 7.99. $C_{17}H_{20}O_2$ required C, 79.65; H, 7.86. δ_H (C_6D_6) 0.10 [3H, s, 5-CH_3(eq)], 1.26 [3H, s, 5-CH_3(ax)], 1.90 [3H, s, 2-CH_3(eq)], 3.25 (2H, d, J = 11.1 Hz, H_{eq}-4, H_{eq}-6), 3.39 (2H, d, J = 11.1 Hz, H_{ax}-4, H_{ax}-6), aromatic protons at 7.26-7.42 (3H, overlapped peaks), 7.62 (1H, d, J = 8.1 Hz), 7.68 (1H, d, J = 8.3 Hz), 7.82 (1H, dd, J =7.6, $J' \approx 1.1$ Hz), 9.07 (1H, d, J = 8.8 Hz). δ_C (C_6D_6) 21.28 [Me(eq)-5], 22.89 [Me(ax)-5], 29.21 (C-5), 30.96 [Me(eq)-2], 71.39 (C-4, C-6), 101.63 (C-2), 125.03, 125.38, 125.93, 126.17, 126.66, 128.98, 129.13 (tertiary aromatic carbon atoms), 131.70, 135.09, 136.46 (quaternary aromatic carbon atoms).

2,5,5-Trimethyl-2-β-naphtyl-1,3-dioxane 4. White crystals, m.p. 91-92 °C, 7.04 g (0.0275 mol) yield 55 %. Found: C, 79.81; H, 7.74. $C_{17}H_{20}O_2$ required C, 79.65; H, 7.86. δ_H (C_6D_6) 0.23 [3H, s, 5-CH_3(eq)], 1.25 [3H, s, 5-CH_3(ax)], 1.80 [3H, s, 2-CH_3(eq)], 3.35 (2H, d, J = 10.2 Hz, H_{eq}-4, H_{eq}-6), 3.49 (2H, d, J = 10.2 Hz, H_{ax}-4, H_{ax}-6), aromatic protons at 7.27-7.29 (2H, overlapped peaks), 7.65-7.74 (4H, overlapped peaks), 8.09 (1H, s). δ_C (C_6D_6) 21.35 [Me(eq)-5], 22.79 [Me(ax)-5], 29.58 (C-5), 32.22 [Me(eq)-2], 71.52 (C-4, C-6), 100.41 (C-2), 124.78, 125.95, 126.01, 126.11, 127.67, 128.17, 128.61 (tertiary aromatic carbon atoms), 133.24, 133.81, 139.10 (quaternary aromatic carbon atoms).

2-Bromomethyl-5,5-dimethyl-2-*ortho*-nitrophenyl-1,3-dioxane 5. White crystals, m.p. 105-106 °C, 6.02 g (0.0182 mol) yield 73 %. Found: C, 47.63; H, 4.99; Br, 24.21; N, 4.44. $C_{13}H_{16}BrNO_4$ required C, 47.41; H, 4.90; Br, 23.99; N, 4.26. δ_H (C_6D_6) -0.01 [3H, s, 5-CH_3(eq)], 1.12 [3H, s, 5-CH_3(ax)], 3.06 (2H, d, J = 11.0 Hz, H_{eq}-4, H_{eq}-6), 3.17 (2H, d, J = 11.0 Hz, H_{ax}-4, H_{ax}-6), 3.81 [2H, s, 2-CH_2Br(eq)], 6.68 [1H, dt (overlapped ddd), $J \approx J' \approx$ 7.9, J'' = 1.2 Hz, H-5'), 6.79 (1H, dd, J = 7.9, J' = 1.1 Hz, H-6'), 6.88 [1H, dt (overlapped ddd), $J \approx J' \approx$ 7.9 Hz, J'' = 1.2 Hz, H-4'), 7.29 (1H, dd, J = 7,9, J' = 1.1 Hz, H-3'). δ_C (C_6D_6) 20.81 [Me(eq)-5], 22.21 [Me(ax)-5], 29.09 (C-5), 38.83 [$BrCH_2$(eq)-2], 72.15 (C-4, C-6), 97.73 (C-2), 123.27, 129.84, 130.00, 130.91 (tertiary aromatic carbon atoms), 128.47 (C-1'), 150.78 (C-2').

2-Bromomethyl-5,5-dimethyl-2-*metha*-nitrophenyl-1,3-dioxane 6. White crystals, m.p. 109-110 °C, 5.85 g (0.0177 mol) yield 71 %. Found: C, 47.33; H, 4.78; Br, 24.20; N, 4.14. $C_{13}H_{16}BrNO_4$ required C, 47.41; H, 4.90; Br, 23.99; N, 4.26. δ_H (C_6D_6) 0.09 [3H, s, 5-CH_3(eq)], 1.15 [3H, s, 5-CH_3(ax)], 2.96 (2H, d, J = 10.9 Hz, H_{eq}-4, H_{eq}-6), 3.12 (2H, d, J = 10.9 Hz, H_{ax}-4, H_{ax}-6), 3.13 [3H, s, 2-CH_2Br(eq)], 6.75 [1H, t (overlapped dd), $J \approx J' \approx$ 8.0 Hz, H-5'), 7.29 [1H, d, J = 8.0 Hz, H-6'), 7.77 (1H, dd, J = 8.0, J' =1.8 Hz, H-4'), 8.28 [1H, t (overlapped dd), $J \approx J' \approx$ 1.8 Hz, H-2']. δ_C (C_6D_6) 21.04 [Me(eq)-5], 22.36 [Me(ax)-5], 29.37 (C-5), 39.40 [$BrCH_2$(eq)-2], 71.51 (C-4, C-6), 97.89 (C-2), 122.61, 123.45, 129.24, 133.36 (tertiary aromatic carbon atoms), 139.37 (C-1'), 149.20 (C-2').

2-Bromomethyl-5,5-dimethyl-2-α-naphtyl-1,3-dioxane 7. White crystals, m.p. 59-60 °C, 5.52 g (0.0165 mol) yield 66 %. Found: C, 61.14; H, 5.92; Br, 23.60. $C_{17}H_{19}BrO_2$ required C, 60.91; H, 5.71; Br, 23.83. δ_H (C_6D_6) 0.02 [3H, s, 5-CH_3(eq)], 1.38 [3H, s, 5-CH_3(ax)], 3.25 (2H, d, J = 11.0 Hz, H-4, H-6), 3.27 (2H, d, J = 11.0 Hz, H-4, H-6), 3.60 [3H, s, 2-CH_3(eq)], aromatic protons at 7.20-7.40 (3H, overlapped peaks), 7.60-7.70 (3H, overlapped peaks), 8.85 (1H, d, J = 8.8 Hz) δ_C (C_6D_6) 21.38 [Me(eq)-5], 23.28 [Me(ax)-5], 29.51 (C-5), 40.20 [BrH_2C(eq)-2], 71.85 (C-4, C-6), 101.93 (C-2), 125.28, 125.68, 125.98, 127.06, 127.76, 129.45, 130.60 (tertiary aromatic carbon atoms).

2-Bromomethyl-5,5-dimethyl-2-β-naphtyl-1,3-dioxane 8. White crystals, m.p. 118-120 °C, 6.44 g (0.0192 mol) yield 77 %. Found: C, 60.77; H, 5.81; Br, 23.68. $C_{17}H_{19}BrO_2$ required C, 60.91; H, 5.71; Br, 23.83. δ_H (C_6D_6) 0.10 [3H, s, 5-CH_3(eq)], 1.34 [3H, s, 5-CH_3(ax)], 3.31 (2H, d, J = 10.7 Hz, H_{eq}-4, H_{eq}-6), 3.36 (2H, d, J = 10.7 Hz, H_{ax}-4, H_{ax}-6), 3.45 [2H, s, 2-CH_2Br(eq)], aromatic protons at 7.22-7.28 (2H, overlapped peaks), 7.49 (1H, m), 7.58-7.68 (3H, overlapped peaks), 7.94 (1H, s). δ_C (C_6D_6) 21.09 [Me(eq)-5], 22.78 [Me(ax)-5], 29.51 (C-5), 40.45 [$BrCH_2$(eq)-2], 71.66 (C-4, C-6), 124.98, 126.21, 126.41, 128.25, 129.54 (tertiary aromatic carbon atoms).

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