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Synthesis and Stereochemistry of Some Heterocyclic Saturated Compounds Based on *l-p*-Nitrophenylserinol Skeleton (III). 1,3-Dioxanic Schiff Bases

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Abstract: Synthesis and stereochemical data of the title compounds are described based on original results, not yet reported in the class of *l-p*-nitrophenylserinol, including rearrangements and double Schiff bases.

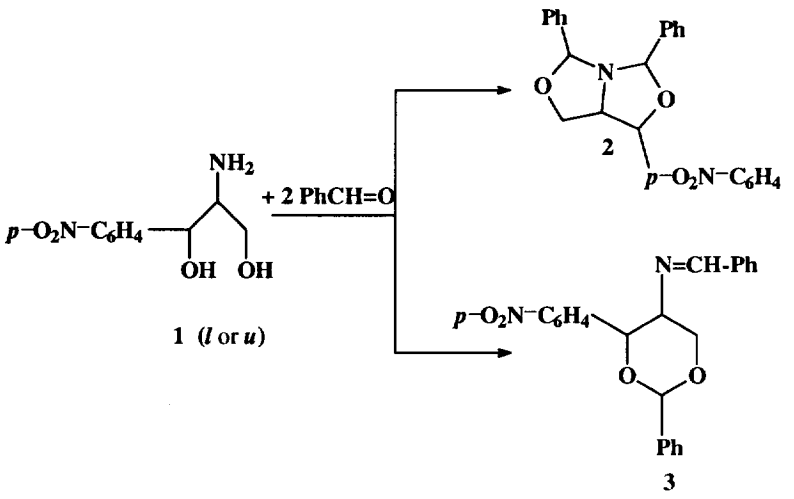
INTRODUCTION

1,3-Dioxanic Schiff bases, as a result of versatile reactivity of *l*- and *u*-2-amino-1-(4-nitrophenyl)-propane-1,3-diol **1**, were just mentioned in the period of '50's in connection with chloromycetine synthesis[1,2]. Thus, in reaction with (substituted)benzaldehydes, in addition to 1-aza-4-(4-nitrophenyl)-2,8-di(substituted)phenyl-3,7-dioxabicyclo[3.3.0]octanes **2**, Pedrazzoli and Tricerri[1] noticed the presence of a side product identified as *2-phenyl-4-(p-nitrophenyl)-5-benzylideneamino-1,3-dioxane* **3 (Scheme 1)** (for reaction with benzaldehyde).We have recently reported some preliminary data on the subject[3] and consider it of interest to enlarge study this aria from both synthetic and stereochemical points of view.

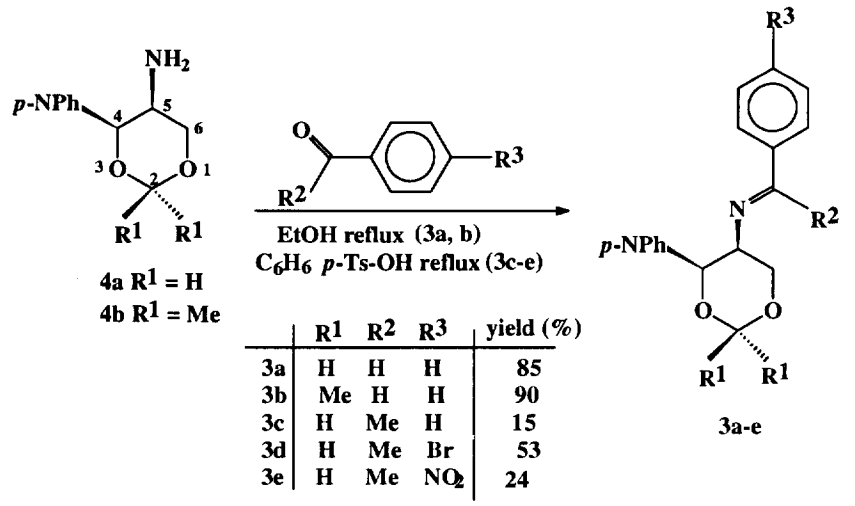
RESULTS AND DISCUSSION

1. Synthesis

As depicted in general **Schemes 2-4,** thirteen dioxanic Schiff bases (where ***p*-NPh** = *p*-nitrophenyl) were prepared by two main routes. All compounds, except **3f,** have not been previously reported[1-4].



Scheme 1

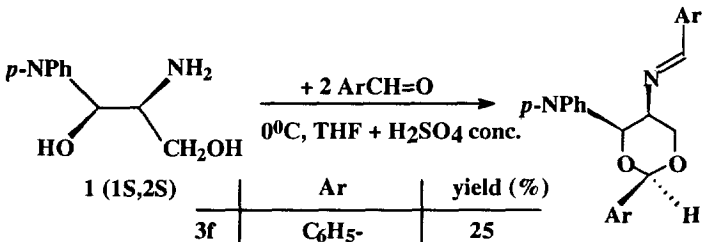


	R1	R2	R3	yield (%)
3a	H	H	H	85
3b	Me	H	H	90
3c	H	Me	H	15
3d	H	Me	Br	53
3e	H	Me	NO_2	24

Scheme 2

Compounds **3a, b, k-m** were easily obtained by refluxing in ethanol, or methanol, stoichiometric amounts of aminodioxanes **4a, b** and (un)substituted benzaldehydes. (Un)substituted acetophenone derivatives **3c-e** were prepared by the method of Senkus[5]. To the best of our knowledge, no condensed compound with alkylphenylketones, having the *l-p*-nitrophenylserinol skeleton has been previously reported. The failure of this type reaction to undergo ring closure has been noted since the pioneering work of Bergmann and Resnik[6] in 1955 but, in 1985, Meslard *et al.*[7] noticed a 4% yield in the reaction between chloromycetine and ethyl-phenyl-ketone to give the corresponding cyclic ketal. In our present work, the aminodioxanes used as starting

material were enantiomeric pure (4*S*,5*S*) **4a**, but racemic (4*S*,5*S* + 4*R*,5*R*) **4b** (in **Schemes 2** and **4** only the 4*S*,5*S* enantiomer of **4b** is depicted). Their syntheses were described elsewhere[4,8]. All compounds **3a-j** were found, by means of NOE-diff. experiments performed optionally on H_{5e} or R^2 (**Table 1**, see **2. Stereochemistry**) to be pure *E*-diastereomers, with regards to the imine double bond. Compounds **3f-j** were synthesised by our published method[4], here extended for more examples (**Scheme 3**).



1 (1S,2S)

	Ar	yield (%)
3f	C_6H_5-	25
3g	*m*-HO-C_6H_4-	34
3h	*o*-O_2N-C_6H_4-	7
3i	*o*-Cl-C_6H_4-	22
3j	α–naphthyl	59

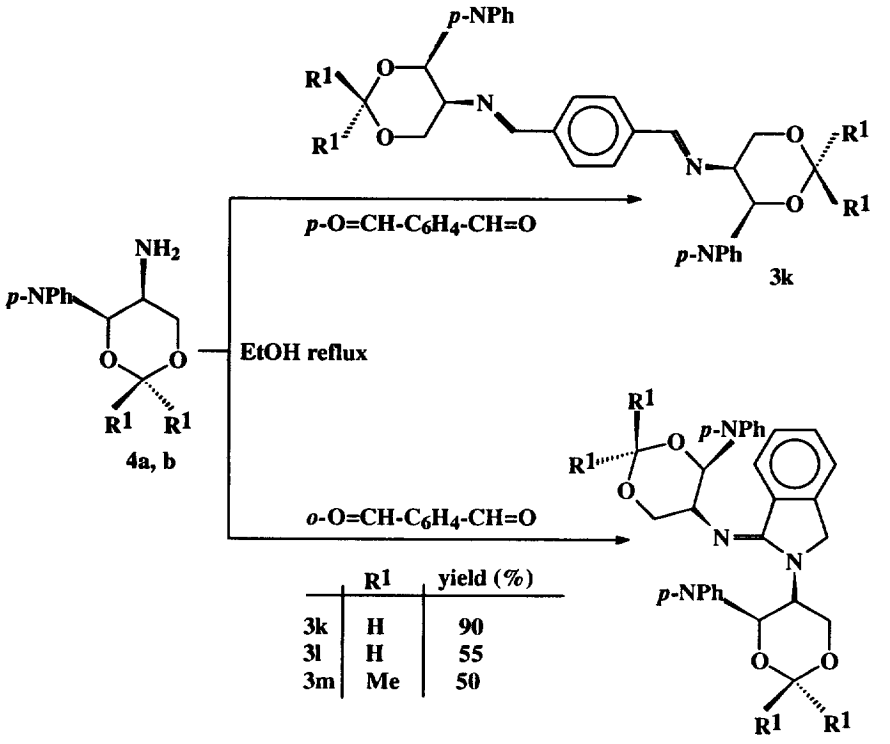
3f-j

Scheme 3

One should observe that they are constitution isomers with their corresponding 1-aza-4-(4-nitrophenyl)-2,8-di(substituted)aryl-3,7-dioxabicyclo[3.3.0]octanes **2** (**Scheme 1**). To avoid cyclization to fused rings, (1*S*,2*S*)-*p*-nitrophenylserinol **1** was first converted to its ammonium salt with 10:1 molar excess of conc. H_2SO_4 (98%, 0°C) and then the reaction mixture was treated dropwise, on cooling (max.0°C), with the stoichiometric amount of the corresponding benzaldehyde as a solution in THF. The nucleophilicity of the amino group was not completely cancelled due to basicity of the THF but it may be assumed that the dioxanic ring-closure preceeded and not succeeded the iminic bond formation. Yields were small eventhough TLC-monitoring showed the reaction complete (with some traces of fused-rings structures **2**). This can be explained by the rapid hydrolysis that occurred when the reaction mixtures were worked up. All dioxanic Schiff bases **3f-j** were pure (*E*-2*R*,4*S*,5*S*) diastereomers according to successive NOE-diff. experiments.

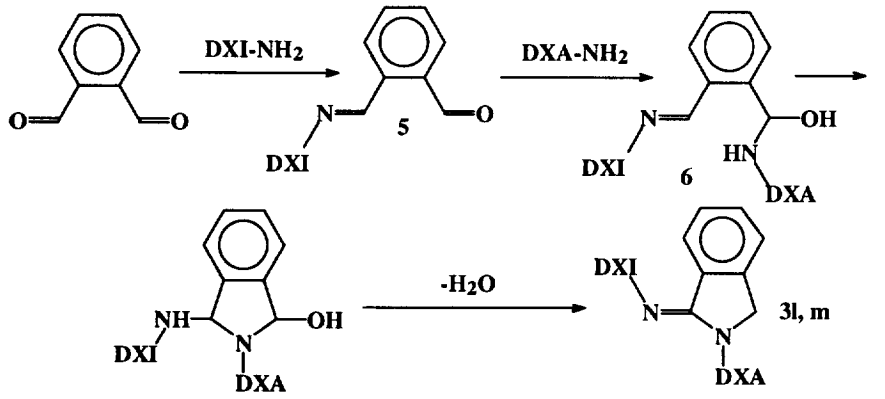
The synthesis of double dioxanic Schiff bases **3k-m** was straight forward (**Scheme 4-6**).

Structures deriving from enantiomerically pure aminodioxane **4a** were isolated as pure diastereomers **3k**, **l** (*E*-4*S*,5*S*). The racemic compound **3m** (from racemic **4b**) was of the same type as **3l** (one pair of pure enantiomers *S,S* + *S,S* and *R,R* + *R,R*) suggesting that only the starting aminodioxanes identically configured at C^4 and C^5 were able to give the isoindolyne condensed system of **3l, m** type.The unexpected formation of a pyrroline ring closure can be suggested by the sequence depicted in **Scheme 5**. Thus, formation, in a first step,



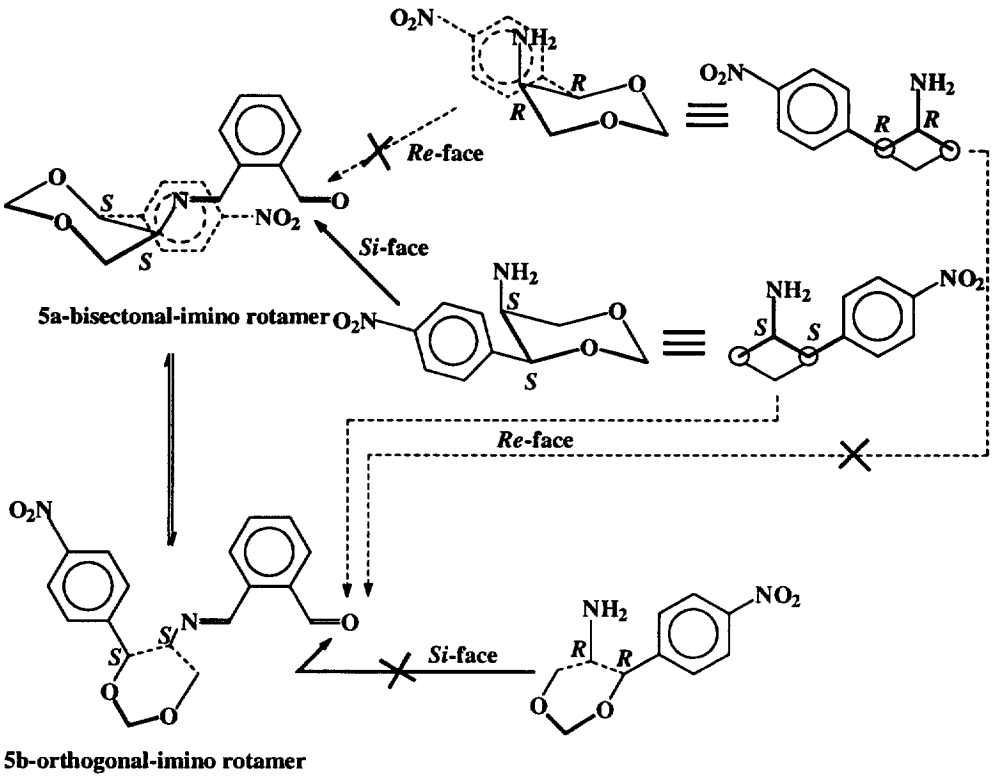
	R1	yield (%)
3k	H	90
3l	H	55
3m	Me	50

Scheme 4



DX represents the dioxane- 5-yl group derived from **4a** or **4b**; I and A represent the two different environments of the dioxane rings in the final structure**I** - Iminodioxane and: **A** - Aminodioxane

Scheme 5



Scheme 6

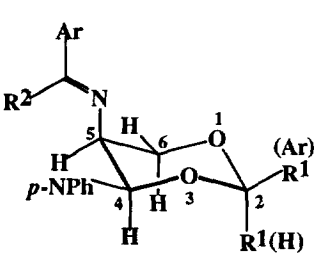
of a mono Schiff base **5** needs no comment. It is to observe however, that *o*-phtaldialdehyde has its both carbonyl groups with enantiotopic faces. Then, if the mono Schiff base rises only the diastereoselectivity problem (*E* or *Z*), the second step, (reaction with **DXA-NH$_2$**) can be sterically influenced by the previous chiral substituent **(DXI) (Scheme 6).** Moreover, the mono Schiff base **5** should be *E*-diastereomer because no *Z*-diastereomer was detected in any of the compounds investigated. As depicted in **Schemes 5, 6** the key step is the nucleophilic attack of the second amino group on the diastereotopic faces of **5.** In the case of pure enantiomeric (4*S*,5*S*) aminodioxane **4a**, the condition that both dioxane units **(DXI** and **DXA)** should be identically configured is *a priori* accomplished. However, if both main rotamers **5a, b** are considered as main substrates, **5a** may be attacked on *Si*-face and **5b** on *Re*-face, and consequently, a pair of diastereomers would be formed (aminal **6**). According to **Scheme 5**, this temporary local chirality has no relevant importance because the new chiral center thus born is then cancelled when the substituted pyroline system is realised. These considerations are valid *mutatis mutandis* for the racemic aminodioxane **4b** but if **DXI** is (4*S*,5*S*)-enantiomer **(Scheme 6)** both rotamers **5a, b** are sterically appropriate to (4*S*,5*S*)-**DXA** interaction only.

2. Stereochemistry

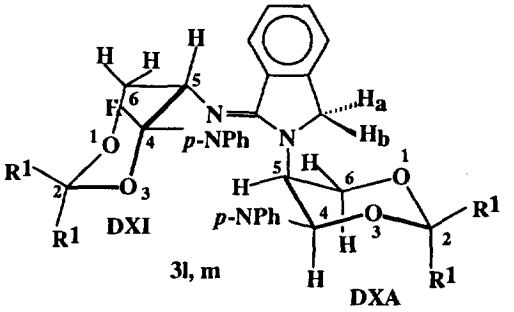
Some stereochemical features[10-12] are worthy of mention, based on high resolution ^{1}H-NMR spectroscopy. Chemical shifts and coupling constants are listed in **Tables 1** and **2** resp.

Table 1: ^{1}H-chemical Shifts* (δ ppm) of the Non-aromatic Protons** of the Dioxanic Schiff Bases **3a-m** and of Aminodioxanes **4a, b**

Proton Compd.	H_{2a}	H_{2e}	H_{4a}	H_{5e}	H_{6e}	H_{6a}	H_{im}	Me (imino)	2-Me (ax.)	2-Me (eq.)
3a	5.09 (d)	5.46 (d)	5.15 (d)	3.51 (d)	4.18 (d)	4.27 (dd)	7.93 (s)	-	-	-
3b	-	-	5.38 (d)	3.55 (d)	3.97 (dd)	4.41 (dd)	7.98 (s)	-	1.58 (s)	1.53 (s)
3c	4.69 (d)	5.37 (d)	4.44 (d)	3.43 (d)	3.92 (d)	3.65 (dd)	-	1.19 (s)	-	-
3d	4.65 (d)	5.28 (d)	4.41 (d)	3.04 (d)	3.71 (t)	3.60 (dd)	-	1.05 (s)	-	-
3e	4.63 (d)	5.27 (d)	4.40 (d)	3.00 (d)	3.67 (d)	3.58 (dd)	-	1.00 (s)	-	-
3f	5.92 (s)	-	5.42 (d)	3.63 (d)	4.37 (dd)	4.52 (dd)	8.07 (s)	-	-	-
3g	5.72 (s)	-	5.30 (s)	2.50 (s)	4.04 (d)	4.26 (d)	9.46 (s)	-	-	-
3h	6.57 (s)	-	5.49 (d)	3.77 (s)	4.37 (dd)	4.57 (dd)	8.48 (s)	-	-	-
3i	6.26 (s)	-	5.46 (d)	3.73 (d)	4.37 (dd)	4.55 (dd)	8.51 (s)	-	-	-
3j	6.37 (s)	-	5.57 (d)	3.74 (s)	4.52 (dd)	4.66 (dd)	8.60 (s)	-	-	-
3k	5.07 (d)	5.45 (d)	5.14 (d)	3.51 (s)	4.17 (d)	4.26 (dd)	7.91 (s)	-	-	-
3l DXI	4.65 (d)	5.25 (d)	4.74 (s)	4.23 (d)	3.53 (dd)	4.15 (d)	-	-	-	-
DXA	4.34 (d)	4.99 (d)	4.51 (s)	4.07 (s)	3.71 (dd)	4.10 (d)	-	-	-	-
3mDXI	-	-	4.77 (d)	4.95 (d)	3.31 (dd)	3.87 (dd)	-	-	1.22 (s)	1.48 (s)
DXA	-	-	4.89 (d)	3.94 (d)	3.73 (dd)	4.03 (dd)	-	-	1.45 (s)	1.53 (s)
4a	4.89 (d)	5.23 (d)	4.92 (s)	2.94 (d)	4.04 (dd)	4.12 (dd)	-	-	-	-
4b	-	-	5.15 (s)	2.82 (d)	4.29 (dd)	3.85 (dd)	-	-	1.53 (s)	1.53 (s)



3a-k



3l, m

*Solvents used: **4a, b, 3a-f, 3h-k**: $CDCl_3$; **3g**: DMSO-d_6; **3l, m**: C_6D_6

(s): singlet; d: doublet; (t): triplet; (dd):doublet of doublets; all steric assignments (axial or equatorial) are based on successive NOE-diff. experiments; in the case of compounds **3l, m based also on (H,H)-COSY experiments; additional δ values: $H_{a,b}$ 4.83 and 3.99ppm (**3l**); $H_{a,b}$ 4.65 and 4.31ppm (**3m**); $J_{a\text{-}b}$(gem)=18.0Hz in both compounds **3l, m**.

Table 2: Coupling Constants *J*(H, H, Hz) of the Non-aromatic Protons of the Dioxanic Schiff Bases **3a-m** and the Aminodioxanes **4a, b**

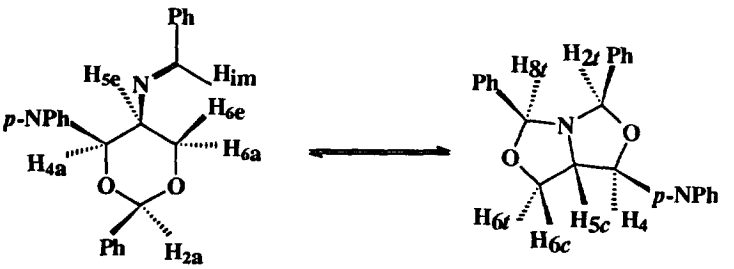
Compound	$J_{2a\text{-}2e}$	$J_{4a\text{-}5e}$	$J_{5e\text{-}6a}$	$J_{5e\text{-}6e}$	$J_{6e\text{-}6a}$
3a	6.3	2.2	2.1	-	11.8
3b	-	2.7	3.4	2.6	12.2
3c	6.2	2.1	2.2	-	11.3
3d	6.2	1.9	2.0	1.0	11.7
3e	6.2	2.1	2.1	-	11.5
3f	-	2.3	2.2	1.3	11.9
3g	-	-	-	-	9.4
3h	-	2.1	2.2	1.0	12.0
3i	-	2.1	2.1	1.0	12.0
3j	-	1.7	1.8	1.2	11.8
3k	6.3	2.1	2.0	-	11.7
3l DXI	6.2	-	3.0	2.4	12.0
DXA	6.2	1.7	-	-	11.5
3m DXI	-	3.1	3.0	1.2	12.2
DXA	-	2.1	2.7	2.0	11.5
4a	6.3	-	2.0	1.3	11.3
4b	-	-	1.8	0.9	11.5

All dioxanic Schiff bases of **3a-m** type are reasonably chair shaped anancomeric structures because of they possess the C^4 *p*-nitrophenyl group which prefers equatorial position[11]. Consequently, the (substituted)arylideneamino group is placed at C^5 in the axial position. This suggests that the conformational free energy of the latter is lower than ΔG = +2.85kcal/mol of the C^4 eq. substituent. Data from **Table 2** allow evaluation of the ring shape on the aliphatic part (C^4, C^5, C^6); thus, the spin system H_{4a}-H_{5e}-H_{6a}-H_{6e} put in evidence in almost all cases the three expected *gauche* vicinal couplings of the proton H_{5e}[11,12].The ratio $^3J_{cis}$/ $^3J_{trans}$ of the AMX (H_{5e}-H_{6a}-H_{6e}) system is about 2.0, and is very close to the same ratio of the unsubstituted 1,3-dioxane, 1.91[11]. Like the 1,3-dioxane itself, compounds **3a-m** are flattened in the aliphatic part with the bulky C^5 substituent pushed back. Geminal coupling patterns are also very similar to the 1,3-dioxane with an expected decrease at C^6 in acetonide structures. It can be noticed that although the molecule is asymmetric, due to the *p*-nitrophenyl group (otherwise it would have a symmetry plane including C^5 and C^2) vicinal *cis*-coupling constants of H_{5e} ($J_{5e\text{-}6a}$ and $J_{5e\text{-}4a}$) are almost equal.

The anisotropy of the iminic system is not responsible for the influence observed concerning the anisochronous C^6 methylene. If R^2 = H, proton H_{6a} is more deshielded than H_{6e} and this fact is only dependent upon the C^2 substituent only (H, aryl or methyl). Thus, $\Delta\delta$ values (ppm) (H_{6a}-H_{6e}) in the series **4a, 3a, 3k** (R^1 = H) are 0.08, 0.09 and 0.08 resp. In the series **3f-3j** [R^1_{eq} = (substituted)aryl, R^1_{ax} = H] the same difference increases to 0.14-0.20ppm, suggesting a long distance influence of the bisectonal aromatic substituent[11]. If R^1 = CH_3 **(4b, 3b)** there again seems to be no influence of the imino group on the anisochronism at C^6 ($\Delta\delta_{a\text{-}e}$=0.44ppm) but the expected steric compression of the axial-methyl group to H_{6a} which is pushed towards the *p*-NPh group. So, the C^2 substituent is responsible for the increase of C^6-methylene anisochronism.

If R^2 = CH_3 (series **3c-e**) there is an obvious *viceversa* difference ($\Delta\delta_{6a\text{-}6e}$= -0.11 to -0.33ppm). This can be explained if free rotation around N(iminic)-C^5 bond is hindered enough for the iminic conjugated system to act as a deshielding factor on H_{6e}.

To estimate more properly the conformational stability of the axial benzylideneamino group (R^2 = H), and in general the stability of the dioxane system bearing this substituent, an equilibration by using compound **3f** (R^1_{eq} = Ph, R^1_{ax} = R^2 = H) was attempted. A Dean-Stark trap was used. In the presence of *p*-Ts-OH acid, in dry benzene under reflux, no reaction took place. As soon as small amounts of benzaldehyde were added, the Schiff base **3f** was partially isomerised to its corresponding (1*R*,2*R*,4*S*,5*S*,8*S*)-1-aza-4-(4-nitrophenyl)-2,8-diphenyl-3,7-dioxabicyclo[3.3.0]octane **7f (Scheme 7).**



3f **7f**

Scheme 7

In **Figure 1** a detail of the ^{1}H-NMR spectrum, heterocyclic protons only, makes it possible to calculate the ratio **3f:7f** = 1: 1.5; the same detail is showed as 2D-(H,H)-COSY experiment **(Figure 2).**

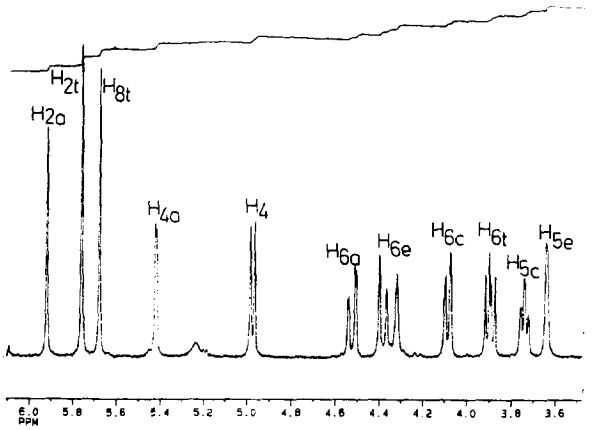


Figure 1: ^{1}H-NMR Spectrum (detail) of the Mixture of Compounds **3f + 7f** (After 15h., Total Time of Equilibration)

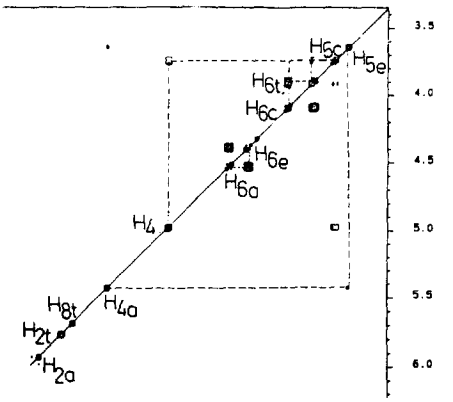


Figure 2: 2D-(H, H)-COSY experiment of the mixture **3f + 7f**

One can observe both AMX systems, well separated, in the regions 4.6-4.3ppm **(3f)** and 4.1-3.9ppm **(7f).** For a better designation, protons belonging to bicycloderivative **7f** were labelled as *cis* (*c*) or *trans* (*t*) regarding the *p*-NPh group that is considered a permanent structural reference. Assignments of these protons were previously discussed[13]. This unusual rearrangement was reasonably clear detected during almost all dioxane ring closures and it seems to be favoured by increasing the temperature. In fact, all **3f-j** compounds were accompanied, in the crude reaction mixture, by their corresponding bicycloderivatives of type **7**. If very crowded aryl substituents were used (e.g. α-naphthyl, **3j**), about equimolar ratio between bicycloderivative of

7j and the dioxane **3j** was found. At least in this series, the greater stability found for the heterocyclic fused-ring system **7** compared with their isomeric dioxanic Schiff bases could be justified by the more free conformations offered by **7** to all three aryl substituents than **3f-j**.This assumption should be correct because no rearrangement was detected with all other dioxanic Schiff-bases here described, for similar conditions **(3a-e).** We note here, however, another particular rearrangement in this class of compounds based on *l-p*-nitrophenylserinol skeleton: its spiropentamethyleneoxazolidine was obtained from the aminospiropentamethylenedioxane, in both solution and in solid state. This rearrangement was previously discussed[8].

The last two compounds **(3l, m)** were more difficult to be assigned than should have been expected. C_6D_6 was used for the best resolution.Combined step by step NOE-diff. and 2D-(H,H)-COSY experiments, as well as the inspection of Dreiding models, revealed that in each compound two distinct dioxanic environments are involved: iminodioxane **DXI** and aminodioxane **DXA** (see also **Scheme 6**). On the other hand, no iminic proton in the appropriate region, but a new AX system (H_a, H_b) in the heterocyclic protons spectral zone was found. In **Figure 3** a significant detail including heterocyclic protons of the compound **3m** is depicted.

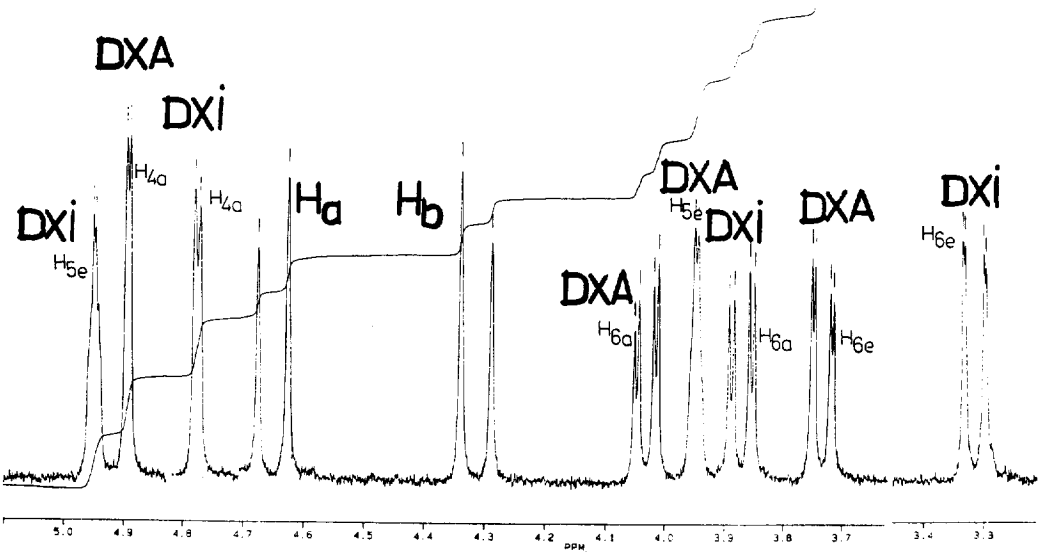


Figure 3: ^{1}H-NMR detail on the heterocyclic protons zone (**3m**)

It can be constantly observed that all peaks consistent with a fixed dioxanic structure are twice present (see δ-values, **Table 1**) and they are quite similar to all other compounds **3a-k**. The unique AX (H_a-H_b) system was assigned to the diastereotopic methylene of the substituted isoindolyne ring. The chirality of the heterocyclic N (as a new asymmetric center that could yield one pair of diastereomers) is expected to be

cancelled as a part of an azomethynic conjugated system (-N=C-N<). This behaviour was confirmed by the fact that both **DXI** and **DXA** are not in relationship as diastereomers, but as distinct parts of a unique structure. Next, NOE-diff. showed clearly that both dioxanic rings are free enough to rotate around C^5-N(imino), C^5-N(amino) bonds for each steric correlation be in the same environment. The most difficult step was to distinguish the two units as amino or imino structures. We believe that the decisive fact consists of the H_{5e} proton environment. From data listed in **Table 1**, its δ-value proves, if iminic structure is assigned to **DXI** (in both **3l, m**), there is a strong deshielding zone (e.g. in **3m**, H_{5e} belonging to **DXI** is the most deshielded, completely different from all series). This can not be justified by the ASIS phenomena only. To compare the magnitude of the aromatic solvent influence, chemical shifts of the aminodioxanes **(4a, b)** *vs.* **DXA (3l, m)** units and those of dioxanic Schiff-bases **(3a, b)** *vs.* **DXI (3l, m)** units should be considered. Thus, all protons except H_{5e} are approximately shielded, without any preference for equatorial or axial position. Then, H_{5e} should be placed in a crowded environment for maximum independence concerning free rotation between **DXI** and **DXA.** That is, we conclude that the most deshielded H_{5e} proton belongs to iminodioxanes designed as **DXI** and the iminic system is the *E*-diastereomer.In this case, H_{5e} is placed in the full deshielding zone of the central benzene ring. Consequently, **DXI** and **DXA** are placed in the less crowded position in comparison to each other.

Obviously, no such problems occur for the double Schiff base **3k** whose dioxanic units exhibited free rotation, proved by the singlet (7.53ppm) assigned to all four aromatic protons of the 1-4 benzylidene group. Moreover, there is no significant difference between chemical shifts and coupling constants of the simple **3a** and double Schiff bases **3k (Table 1, 2).**

CONCLUSIONS

As we have shown, dioxanic Schiff bases having the *l-p*-nitrophenylserinol skeleton are available by using classical methods that make it possible to discriminate between the reactivity of the hydroxyl or amino groups. All compounds are diastereomerically pure and rigid heterocyclic structures. The iminic double bond might offer interesting further investigations to extend the already existing asymmetry. Rearrangements may occur involving dioxanic Schiff bases *vs.* azadioxabicyclooctanes.

EXPERIMENTAL

NMR-spectra were performed on Brucker AM 400 spectrometer (with an Aspect 3000 computer) operating at 400 MHz for ^1H, except compounds **3a, b, f, l, m**, (Brucker 360 MHz spectrometer). No $SiMe_4$ was added; chemical shifts were measured against the solvent peak. Syntheses of compounds **3a, b, f, m, l,**

were described elsewhere[3,4]. Melting points are not corrected. Specific rotations were measured on a Polamat K. Z. Jena instrument.

Synthesis of compounds 3c-e, general procedure:

6.72g (0.03mole) (4*S*,5*S*)-5-amino-4-(4-nitrophenyl)-1,3-dioxane **4a** dissolved in 50ml dry benzene with the equimolar amount of the corresponding (substituted)acetophenone, in the presence of cat. amounts of *p*-Ts-OH are refluxed in a Dean-Stark trap for continuous removal of water. The reaction is monitored by TLC (eluent ligroine:acetone 3:1 v/v, visualisation on I_2 bath). When the starting aminodioxane is detected in small traces only, the reaction mixture is neutralized with excess of anhydrous Na_2CO_3, filtered off and the organic solution is evaporated *in vacuo* on a steam bath. The oily residue is crystallized from ethanol, under reflux. The crude product is further purified from ether, at room temp.

The NMR data are listed in **Tables 1, 2.**

Compound, yield (%), reaction time (h), m.p.(°C), $[\alpha]_D^{20}$(solvent), elemental analysis, as follows:

(*E*)-N-[(4*S*,5*S*)-4-(4-Nitrophenyl)-1,3-dioxane-5-yl]-acetophenonimine 3c: 15; 38; 190-1; + 120 (1% $CHCl_3$). Anal. calcd. for $C_{18}H_{18}N_2O_4$: C 66.25%, H 5.52%, N 8.58%. Found: C 65.90%, H 5.25%, N 8.30%; **(*E*)-N-[(4*S*,5*S*)-4-(4-Nitrophenyl)-1,3-dioxane-5-yl]-4-bromoacetophenonimine 3d**: 53; 41; 149-51; + 112.5 (1% $CHCl_3$). Anal. calcd. for $C_{18}H_{17}BrN_2O_4$: C 53.33%, H 4.19%, Br 19.75%, N 6.91%. Found: C 53.50%, H 3.95%, N 6.62%, Br 20.25%;

(*E*)-N-[(4*S*,5*S*)-4-(4-Nitrophenyl-1,3-dioxane-5-yl]-4-nitroacetophenonimine 3e : 24; 37; 184-6; + 397.5 (1% $CHCl_3$). Anal. calcd. for $C_{18}H_{17}N_3O_6$: C 58.22%, H 4.58%, N 11.32%. Found: C 57.90%, H 4.45%, N 11.22%;

Synthesis of compounds 3g-j, general procedure:

Fine powdered 21.2g (0.1mole) (1*S*,2*S*)-2-amino-1-(4-nitrophenyl)-propane-1,3-diol is portionwise added to 50ml H_2SO_4 98% with vigorous stirring, and the temperature is kept at about 0°C. Stoichiometric amount of (substituted)benzaldehyde is dissolved in 100ml anhydrous THF and the resulted solution is added very slowly to the reaction mixture, with stirring and cooling (max. 0°C) and left stirring at this temperature for 24h.. Finally it is poured portionwise in 1kg. ice with 250ml chloroform and 250ml aqueous NH_3 (25%). During neutralization, vigorous stirring is necessary and the temperature should be kept below 0°C. The final *p*H should be greater than 8. The organic layer is separated and the aqueous solution is twice extracted with 100ml chloroform that are added to the main solution. The combined organic phase is washed repeatedly with 100ml water untul *p*H=7 and dried over anhydrous $MgSO_4$. After filtering, it is evaporated *in vacuo* on a steam

bath to an oily residue that is crystallized from alcohol. The crystalline material is further purified from ether.

NMR data are listed in **Tables 1, 2.**

Compound, yield (%), m.p.(°C, solvent), $[\alpha]_D^{20}$ (solvent), elemental analysis, as follows:

(2*R*,4*S*,5*S*)-5-(*E*)-(3-Hydroxybenzylideneamino)-2-(3-hydroxyphenyl)-4-(4-nitrophenyl)-1,3-dioxane 3g: 34; 229-30 (MeOH); + 38 (1% DMSO). Anal. calcd. for $C_{23}H_{20}N_2O_6$: C 65.71%, H 4.76%, N 6.66%. Found: C 65.90%, H 4.55%, N 6.52%;

(2*R*,4*S*,5*S*)-5-(*E*)-(2-Nitrobenzylideneamino)-2-(2-nitrophenyl)-4-(4-nitrophenyl)-1,3-dioxane 3h: 7; 205-6 (EtOH); + 151 (1% $CHCl_3$). Anal. calcd. for $C_{23}H_{18}N_4O_8$: C 57.74%, H 3.76%, N 11.71%. Found: C 57.50%, H 3.55%, N 12.00%.

(2*R*,4*S*,5*S*)-5-(*E*)-(2-Chlorobenzylideneamino)-2-(2-chlorophenyl)-4-(4-nitrophenyl)-1,3-dioxane 3l: 22; 155-6 (BuOH); + 187 (1% $CHCl_3$). Anal. calcd. for $C_{23}H_{18}Cl_2N_2O_4$: C 60.39%, H 3.93%, Cl 15.53%, N 6,12%. Found: C 59.95%, H 3.75%, N 6.20%, Cl 15.89%;

(2*R*,4*S*,5*S*)-5-(*E*)-(1-Naphthylideneamino)-2-(1-naphthyl)-4-(4-nitrophenyl)-1,3-dioxane 3j: 59; 101-2 (EtOH); + 124 (1% $CHCl_3$). Anal. calcd. for $C_{31}H_{24}N_2O_4$: C 76.23%, H 4.91%, N 5.73%. Found: C 76.15%, H 5.10%, N 5.90%;

1,4-(*E*)-N-[(4*S*,5*S*)-4-(4-Nitrophenyl)-1,3-dioxane-5-yl]-terephthaldiimine 3k:

4.00g (0.0178mole) (4*S*,5*S*)-5-amino-4-(4-nitrophenyl)-1,3-dioxane and 1.20g (0.009mole) terephtaldialdehyde in 50ml methanol are refluxed with stirring for 4h. The crystalline product is filtered off at room temperature to yield 4.80g crude product. After recristallyzation from methanol, 4.40g are obtained (90% yield) as white powder; m.p. 230-5°C (MeOH); $[\alpha]_D^{20}$ +509 (1% $CHCl_3$). Anal. calcd. for $C_{28}H_{26}N_4O_8$: C 61.53%, H 4.76%, N 10.25%. Found: C 61.96%, H 4.50%, N 10.11%. NMR-data see **Table 1, 2.**

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