

Structure and stereochemistry of cyclodimers obtained by acid treatment of *trans*-stilbenes and of *N*-1,2-diarylethylamides

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The reaction of *trans*-stilbenes and *N*-1,2-diarylethylamides with ethyl polyphosphate affords indanes and tetralins with three stereogenic centres. The structural and configurational assignment of the cyclodimers is based mainly on the NMR and MS data. A possible transition state for the reaction is discussed.

In several communications we have reported that ethyl polyphosphate (EPP) can act on type I amides as a satisfactory and mild cyclodehydration agent to produce dihydroisoquinoline (DHIQ) and also as an effective deamidation reagent to produce *trans*-stilbenes. Furthermore, we have reported that in some cases cyclodimeric derivatives were obtained as well as *trans*-stilbenes (Scheme 1).¹ Our previous results, summarised in Table 1, show that the course of the reaction depends mainly on the substituents present in the aromatic rings of the starting amides. We have also documented that the reaction of some *N*-acyl-1-arylalkylamines with EPP yields styrenes, but that in some cases only phenylindanes may be isolated² (Table 1). Again, cyclodimerisation depends on the degree and type of benzene ring substitution.

The cyclodimerisation of stilbenes and styrenes, with acidic reagents, has been widely described in the literature,^{3–8} but though there are no differences of opinion about the preparation of indane structures starting from styrenes, the situation is not clear in the case of the dimerisation of stilbenes where the formation of indanes, tetralins (1,2,3,4-tetrahydronaphthalenes) and open dimers has been reported. Walker⁹ in 1954 and Battersby and Binks¹⁰ in 1958 were the first in reporting the preparation of a dimer of *trans*-3,3',4,4'-tetramethoxystilbene originated from *N*-[1,2-bis(3,4-dimethoxyphenyl)ethyl]acetamide subjected to the conditions of the Bischler–Napieralsky (B–N) reaction; however, they failed to indicate the structure of

the dimer. After that several authors, by treatment of *cis*- and of *trans*-stilbene in different acidic conditions, have reported the formation of cyclodimerisation products of the 1-benzylindane type, trisubstituted tetralins and trimeric products.^{6,7,11,12} As a rule, published data prove to be incomplete and even contradictory, particularly as concerns the stereochemistry of the final product.

The present work describes how, on the basis of spectroscopic data, it has been possible to perform structural assignment and to determine the stereochemistry of a series of cyclodimers (CDs), indanes and tetralins with three stereogenic centres, obtained starting from some *N*-acyl-1,2-diarylethylamines and *trans*-stilbenes with EPP (Table 2, Scheme 2). The probable mechanism leading to cyclodimerisation products is also discussed: indanes *versus* tetralins.

Structural assignment of the cyclodimers

The amides 1–6 and the *trans*-stilbenes 7–9 (Table 2, Scheme 2) were treated with EPP at 80 °C for 8 h. Again it was observed that the course of the reaction is modified by the substituents as depicted in Scheme 1, as follows.

a) The prevalence of the “retro-Ritter” reaction (*via* A) when the aryl group attached to the C-β is not nucleophilic enough in the cyclisation position.

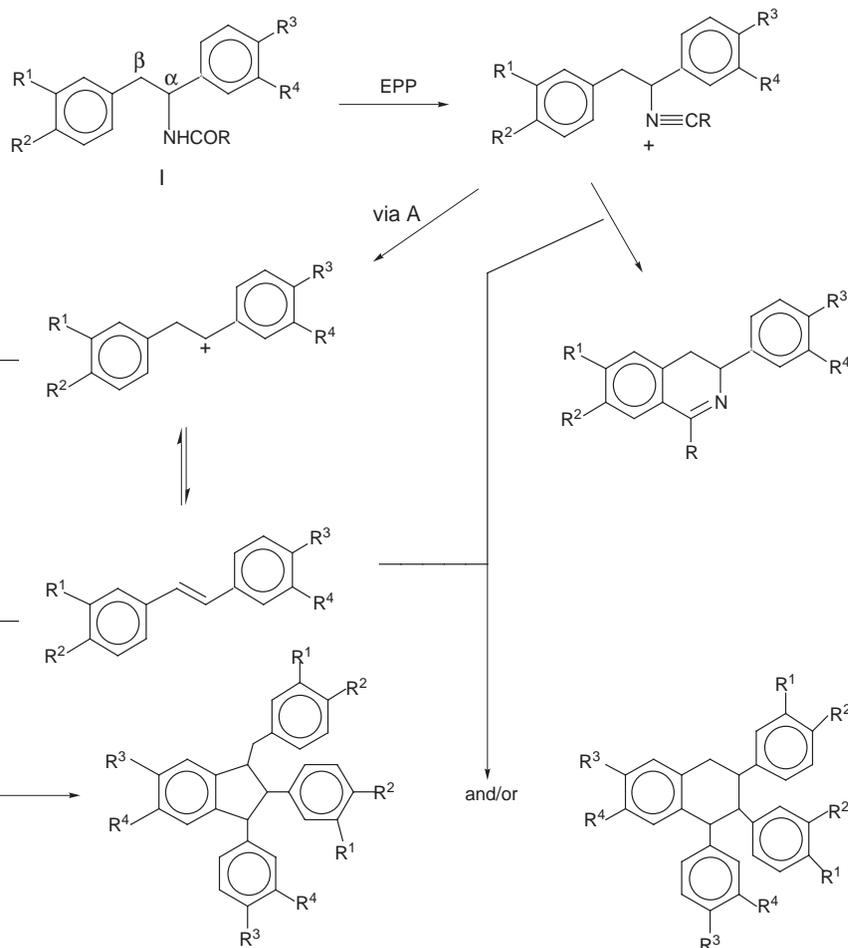
b) Whenever the “retro-Ritter” reaction affords a *trans*-

Table 1 Reaction products of amides with EPP

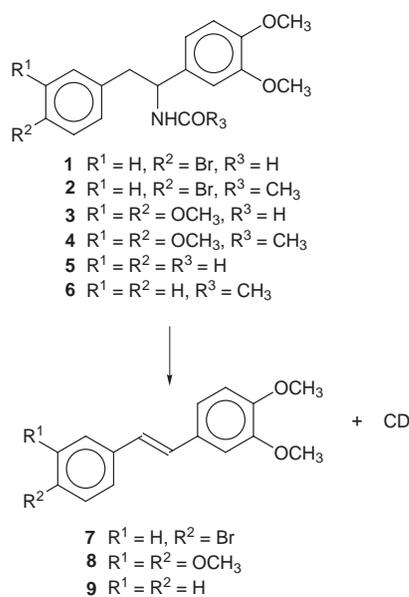
Entry	Amide	Dihydroisoquinoline (%)	Styrene or stilbene (%)	Indanes (%)	Tetralins (%)	Ref.
1	PhCHRCH ₂ Ph		77			1(b)
2	PhCHRCH ₂ An		71			1(b)
3	PhCHRCH ₂ Ver	89				1(b)
4	PhCHRCH ₂ Pip	85				1(b)
5	AnCHRCH ₂ Ph		78			1(b)
6	AnCHRCH ₂ An		82			1(b)
7	AnCHRCH ₂ Ver	8	10		37 ^a	1(b)
8	VerCHRCH ₂ An		33		50 ^a	1(b)
9	VerCHRCH ₂ 4-NO ₂ Ph		80	7 ^b		1(b)
10	4-NO ₂ PhCHRCH ₂ Ver	70	7			1(b)
11	AnCHRCH ₂ C ₆ H ₁₁		48			2
12	3-AnCHRCH ₂ CH ₃		51			2
13	VerCHRCH ₃			56 ^c		2
14	VerCHRCH ₂ CH ₃			56 ^d		2
15	PipCHRCH ₂ CH ₃			78 ^e		2

R: NHCHO, Ph: phenyl, An: 4-methoxyphenyl, Ver: 3,4-dimethoxyphenyl, Pip: 3,4-methylenedioxyphenyl. ^a Mixture of regio- and stereoisomers.

^b Mixture of stereoisomers. ^c Isomer: *r*-1-methyl-*c*-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane. ^d Isomer: *r*-1-ethyl-*c*-2-methyl-*t*-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane. ^e Isomer: *r*-1-ethyl-*c*-2-methyl-*t*-3-(3,4-methylenedioxyphenyl)-5,6-methylenedioxyindane.



Scheme 1



Scheme 2

stilbene with at least one aryl ring by the substitution of a 3,4-dimethoxyphenyl group, a mixture of diastereoisomeric cyclodimers may be isolated.

The MW of the compounds isolated in every case duplicates the value of the corresponding stilbenes. The possible structures of these compounds would be those indicated as **10**, **11**, **12**, **13** and **14** (Fig. 1). The ^{13}C -NMR spectra show the presence of four sp^3 carbon atoms, while DEPT experiments indicate that three of these are tertiary carbons and one secondary. These data allow structures **10**, **11** and **12** to be ruled out, but they fail

Table 2 Reaction products of amides and stilbenes with EPP

Compound	Stilbene (%)	Indanes (%)	Tetralins (%)
VerCHR ¹ CH ₂ 4-BrPh (1)	25 (7)	53 (7-I , 7-II)	
VerCHR ² CH ₂ 4-BrPh (2)	26 (7)	67 (7-I , 7-II)	
VerCH=CH4-BrPh (7)		65 (7-I , 7-II)	
VerCHR ¹ CH ₂ Ver (3)			99 (8-I)
VerCHR ² CH ₂ Ver (4)			99 (8-I)
VerCH=CHVer (8)			97 (8-I)
VerCHR ¹ CH ₂ Ph (5)	20 (9)	45 (9-I , 9-II , 9-III)	
VerCHR ² CH ₂ Ph (6)	30 (9)	48 (9-I , 9-II , 9-III)	
VerCH=CHPh (9)		41 (9-I , 9-II , 9-III)	

R¹: NHCHO, R²: NHCOCH₃, Ph: phenyl, Ver: 3,4-dimethoxyphenyl.

to discriminate between **13** and **14**. The choice between structures **13** and **14** was made on the basis of the following data:

a) Gusten and Schulte-Frohlinde reported¹² that in the mass spectra of 1-benzylindanes the base peak originates from the loss of the benzyl group, while in the case of the tetralins it derives from a retro Diels–Alder type cleavage. Table 3 indicates the cleavage types presented by the CDs isolated in our reactions that would show the presence of the two types of carbon skeletons;

b) another finding taken into account for the structural assignment originates from the values of the geminal coupling constants of the benzyl methylene hydrogen atoms; the value found in the literature¹³ is of the order of 13 Hz for the exocyclic benzyl groups and 16 Hz for the endocyclic benzyl groups (Table 4). Besides, we have recently reported the stereodirected synthesis of the four racemic diastereoisomers of 1-benzyl-2,3-diphenylindane,¹⁴ and chemical shift data of the carbon atoms are listed in Table 5, which will be used as model compounds;

c) the correlation spectra H/C: HETCOR and COLOC.

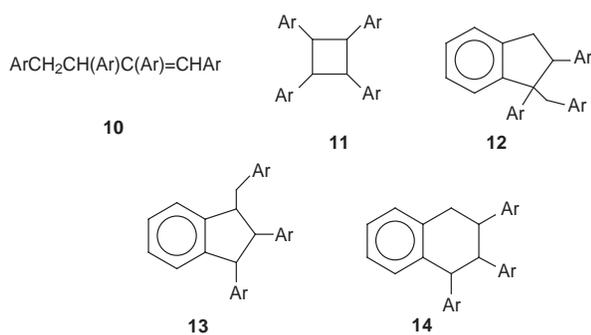
Table 3 Mass spectra: comparative data of cyclodimers of stilbenes

	M ⁺	M ⁺ /2	M ⁺ – Bz	M ⁺ – Bz – Ar
1,2,3-Triphenyltetralin ^a	360 (3)	180 (100)	269 (11)	191 (8)
1-Benzyl-2,3-diphenylindane ^a	360 (19)		269 (100)	191 (47)
CD 7-I	640 (7.5)		469 (100)	329 (10.5)
	638 (13.8)		467 (98.9)	331 (10.2)
	636 (7.3)			
CD 7-II	640 (1.5)		469 (95.5)	329 (18.0)
	638 (3.4)		467 (100)	331 (17.0)
	636 (3.6)			
CD 8-I	600 (9.3)	300 (48.0)	449 (10.1)	
		↓ -31		
		269 (100)		
CD 9-I	480 (17.1)		389 (100)	251 (40.3)

Bz: C₆H₅CH₂; 4-Br- C₆H₄CH₂; 3,4-(CH₃O)₂ C₆H₃CH₂. Ar: C₆H₅; 4-Br- C₆H₄; 3,4-(CH₃O)₂ C₆H₃. ^a Reference 12.

Table 4 Cyclodimers of stilbenes: ¹H-NMR data of aliphatic protons

	H-1	H-2	H-3	CH ₂
CD 7-I	3.54 m	3.87 m	4.62 d	2.31 dd 2.46 dd
		<i>J</i> _{2,3} = 9.8		<i>J</i> _{gem} = 13.3
				<i>J</i> _{CH₂,H1} = 5.4; <i>J</i> _{CH₂,H1} = 10.8
CD 7-II	3.85 m	3.01 m	4.14 d	2.92 m
		<i>J</i> _{2,3} = 9.2		
CD 8-I	4.16 d	3.05 dd	3.36 m	3.21 dd 3.06 dd
	<i>J</i> _{1,2} = 10.3	<i>J</i> _{2,3} = 11.5		<i>J</i> _{gem} = 15.7
				<i>J</i> _{3,4a} = 4.1; <i>J</i> _{3,4b} = 11.5

**Fig. 1**

In the particular case of the CD 7-I the mass spectrum shows a base peak for M⁺ – Bz; the value of the coupling constant of the benzyl methylene group is *J*_{gem} 13.3; the HETCOR spectrum indicates the correlation to ¹*J* of ¹H-¹³C-NMR: 2.31 and 2.46 (CH₂)/36.7; 3.54 (H-1)/49.9; 4.62 (H-3)/52.8 and 3.87 (H-2)/59.6. Lastly, the COLOC spectrum showed correlation between the hydrogen atoms of the benzyl methylene group with one of the quaternary aromatic carbon atoms (136.3) and with one of the tertiary aromatic carbon atoms (131.2) of a 4-bromophenyl group (Fig. 2). All these data allow the 1-benzylindane structure to be assigned unequivocally to compound 7-I and by analogy to compound 7-II (Fig. 3). In the mass spectrum of CD 8-I a M⁺/2 cleavage is observed which is characteristic of the tetralin structures (Table 3); the geminal coupling constant of the benzyl methylene hydrogen atoms is *J* 15.7; the HETCOR spectrum indicates the following correlation to ¹*J* of ¹H-¹³C-NMR: 3.06 and 3.21 (CH₂)/38.9; 3.36 (H-3)/54.1; 4.16 (H-1)/45.8 and 3.05 (H-2)/55.4. Lastly, there is a marked difference between the ¹³C spectrum of this CD and the ¹³C spectra corresponding to the four model CDs (Table 5). Taken jointly, these data indicate that the structure of a 1,2,3-triaryltetralin should be assigned to compound 8-I. CDs 9-I and 9-II formed from *N*-acyl-[1-(3,4-dimethoxyphenyl)-2-phenylethyl]amine (amides 5 and 6, Table 2) and from the *trans*-3,4-dimethoxy-stilbene were assigned the indane structure and 9-III that of

Table 5 Cyclodimers of stilbenes: ¹³C-NMR data of aliphatic carbons

	C-1	C-2	C-3	CH ₂
1-Benzyl-2,3-diphenylindanes ^a				
(α) <i>r</i> -1, <i>c</i> -2, <i>t</i> -3	50.6	59.4	53.3	36.9
(β) <i>r</i> -1, <i>c</i> -2, <i>c</i> -3	50.1	58.8	56.8	34.7
(γ) <i>r</i> -1, <i>t</i> -2, <i>c</i> -3	51.9	63.4	59.4	39.6
(δ) <i>r</i> -1, <i>t</i> -2, <i>t</i> -3	49.0	56.8	55.6	39.3
Cyclodimers				
CD 7-I	49.9	59.6	52.8	36.7
CD 7-II	51.5	62.6	59.1	39.9
CD 8-I	54.1	55.4	45.8	38.9
CD 9-I	50.5	60.5	52.7	37.5
CD 9-II	51.4	63.3	58.8	39.9
CD 9-III	54.9	56.9	46.2	39.9

^a Reference 14.

tetraline. This assignment was made on the basis of the comparison of their ¹³C-NMR spectra (Table 5).

Configurational assignment of the cyclodimers

Stereochemical assignment of the CDs was made taking into account the coupling constants in the ¹H-NMR spectra and chemical shifts of the benzyl methylene carbon atoms. The configuration of indane structures 7-I and 7-II was achieved on the basis of the *J*_{2,3} value which in both corresponds to a *trans* configuration (*J* 9.8 and 9.2, respectively, Table 4) and of the chemical shift value of the methylene carbon atom (36.7 and 39.9 ppm, respectively, Table 5), which indicate a marked protective γ effect in one of the isomers, thus showing a *cis* relationship between the benzyl group in C-1 and the aryl group linked to C-2. Besides, the comparison of the chemical shifts of C-1, C-2, C-3 and CH₂ agrees with indane models α and γ (Table 5). Therefore, isomer 7-I has a 1,2-*cis*,2,3-*trans* and 7-II a 1,2-*trans*,2,3-*trans* configuration (Fig. 3). Tetralin 8-I was assigned the configuration 1,2-*trans*,2,3-*trans* by taking into account the values of the coupling constants *J*_{1,2} 10.3 and *J*_{2,3} 11.5 (Table 4). Configuration assignment of the CDs 9-I to 9-III

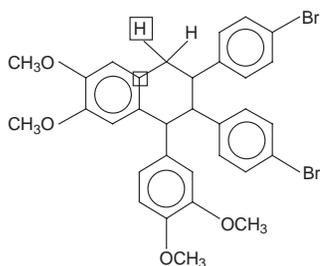
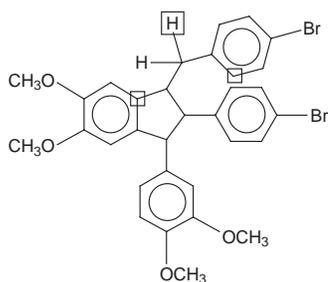
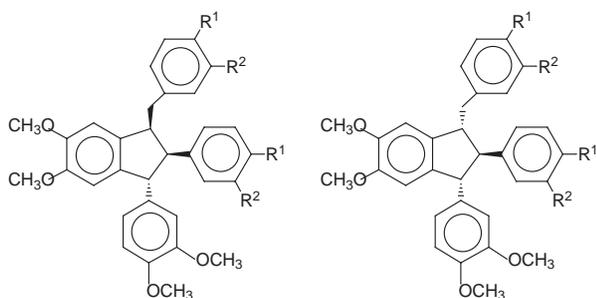
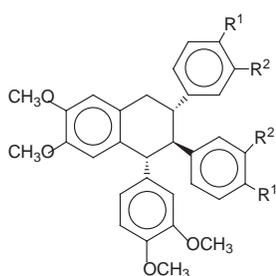


Fig. 2



7-I $R^1 = \text{Br}, R^2 = \text{H}$
 9-I $R^1 = R^2 = \text{H}$

7-II $R^1 = \text{Br}, R^2 = \text{H}$
 9-II $R^1 = R^2 = \text{H}$



8-I $R^1 = R^2 = \text{OCH}_3$
 9-III $R^1 = R^2 = \text{H}$

Fig. 3

arises from the comparison of ^{13}C -NMR spectrum data (Table 5): **9-I**, 1,2-*cis*,2,3-*trans*; **9-II**, 1,2-*trans*,2,3-*trans*; and **9-III**, 1,2-*trans*,2,3-*trans* (Fig. 3).

Formation of the 5-membered versus the 6-membered ring. Mechanisms of cyclodimerisation and source of stereocontrol

Assuming that the process of cyclodimerisation to a 1-benzylindane or to a trisubstituted tetralin is carried out starting from a dimeric carbocation, it would be possible to explain the dissimilar course of this reaction (Scheme 4).² Dimeric carbocations could be formed by the attack of *trans*-stilbene on the intermediary nitrilium ion (B-N) or from two molecules of *trans*-stilbene by acid treatment. In the cases studied the substrates have at least one aryl group with a 3,4-dimethoxyphenyl type substitution, thus leading to the carbocations in

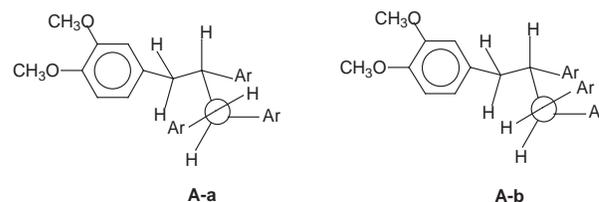
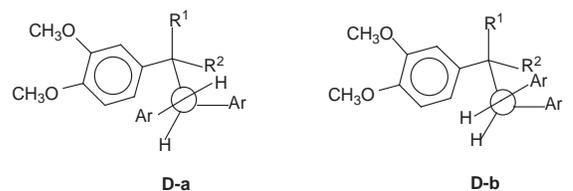
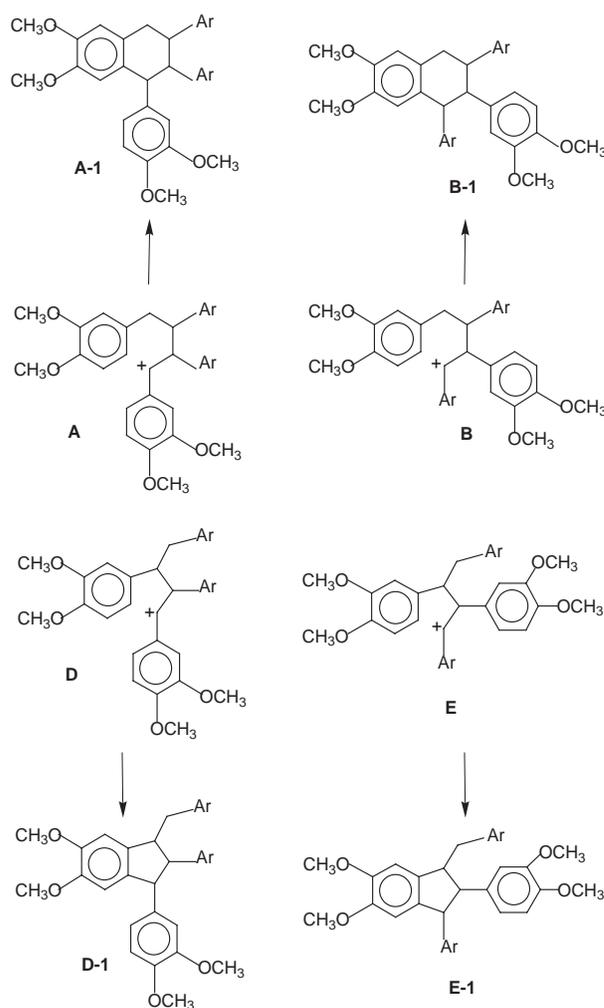
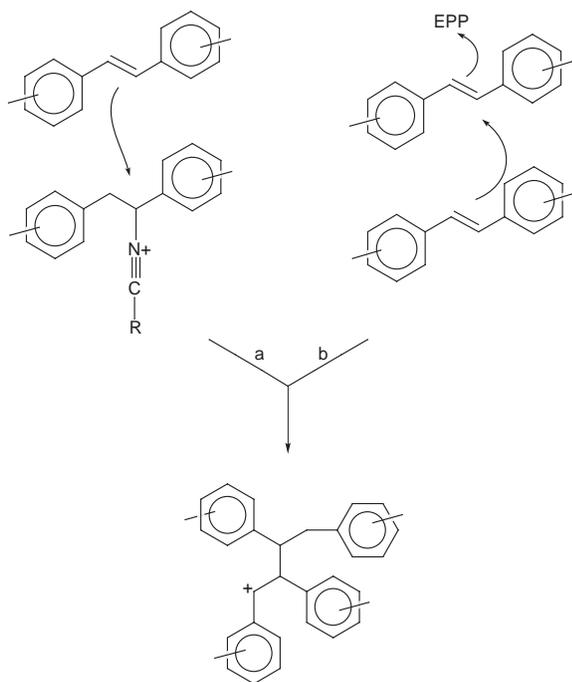


Fig. 4



Scheme 3

Scheme 3. Considering the structural differences of the aryl groups (Ar = phenyl; 3,4-dimethoxyphenyl; and 4-bromophenyl) linked to the carbon atom with the positive charge, it may be assumed that carbocations **A** and **D** possess greater capacity to be formed as compared to **B** and **E** due to the fact that the positively charged carbon atom is substituted by a 3,4-dimethoxyphenyl group. Electron-donor methoxy groups contribute to its greater stability. Thus, the CDs that should be formed are those indicated by **A-1** and/or **D-1** structures, but if the aryl group should provide a 4-methoxyphenyl, for instance, then structures **B-1** and **E-1** would be formed. On the other hand, regardless of the route leading to the carbocation



Scheme 4

(Scheme 4), the benzyl carbon atom that provides the bond forming the dimeric moiety **A**, **B**, **D** or **E** should be the one which in the transition state could sustain more efficiently a positive charge. Lastly, the “monomer” stilbene would contribute to such a bond the carbon atom that allows the formation of the more stable carbocation. These considerations explain the CDs obtained in each reaction. CD **8-I** possesses a trisubstituted tetralin structure. In this case there is only a single carbocation since all the aryl groups are equivalent, so that the more stable 6-membered ring tends to be formed. In the preparation of CDs **7-I** and **7-II** the carbocations with greater stability are **A** and **D**. However, carbocation **A** would be in a low yield because the “monomer” condensation step is not favoured, since the aryl moiety is a 4-bromophenyl group; therefore, the product obtained is the one which originates from **D** cyclisation. CDs **9-I**, **9-II** and **9-III** provide an intermediate case. The aryl moiety is a phenyl group, which facilitates the formation of both carbocations **A** and **D** and cyclisation leads similarly to five- and to six-membered rings.

Compounds **7-I** and **7-II** have an identical C-2/C-3 configuration (*trans*). A possible explanation is to assume that in the dimeric carbocation **D** the steric effect of the voluminous aryl group linked to the sp^2 carbon atom is smaller for conformer **D-a** than for **D-b** (Fig. 4) and this arrangement would be independent of the stereoisomeric relationship of the future C-1 and C-2 atoms. An identical situation occurs in the preparation of trisubstituted tetralin **8-I** with the 1,2-*trans*,2,3-*trans* configuration, where conformer **A-a** of carbocation **A** is that of lesser steric interaction.

It may be observed in compounds **7-I** and **7-II**, as well as in compounds **9-I** and **9-II**, that the configuration between substituents linked to the C-1 and C-2 atoms is preferably *cis*, indicating that the formation of the more favoured intermediate cyclodimeric cation is the one which leads to such stereoisomeric relationships, as also happens when indanes are obtained from styrenes. In all studied cases, the substituent linked to the stereogenic centre formed in the cyclisation step presents a *trans* relationship with respect to the substituent present on the neighbouring carbon.

Conclusions

It may be concluded that, in the studied cases, the ring size

formed in cyclodimerisation is determined by the substituents present in the aryl group linked to the C-1 atom of the starting amide. Thus, strong electron-donor substituents lead to a 6-atom ring (Table 2, compounds **3**, **4** and **8**), while electron-acceptor substituents lead to a 5-atom ring (Table 1, entry 9 and Table 2, compounds **1**, **2** and **7**). Lastly the phenyl group leads to cyclodimers with both ring sizes (Table 2, compounds **5**, **6** and **9**).

Experimental

General

The ^1H - and ^{13}C -NMR spectra were recorded with a Bruker WP 80 SY FT spectrometer with CDCl_3 as solvent, employing Me_4Si as internal standard (δ 0.00). Two dimensional spectra were recorded on a Bruker AC-300 instrument by using standard Bruker software. Mass spectra were obtained by direct injection of the sample as chloroform solutions by using a Shimadzu GCQP 1000 mass spectrometer operating at an ionising electron energy of 70 eV. Infrared spectra were obtained on Shimadzu IR 440 spectrometer. Elemental analyses were carried out in our laboratories with a Coleman Analyser. Melting points (uncorrected) were obtained with a Thomas Hoover apparatus. Preparative thin-layer chromatography (PTLC) was performed on a 20×20 cm glass plate coated with silica gel 60 F254 (0.50 mm).

Synthesis of the *N*-(1,2-diarylethyl)amides

The amides **3**, **4**, **5** and **6** were prepared as described previously.^{15,16} The amides **1** and **2** were prepared from ethanone **15** according to the literature.²

1-(3,4-Dimethoxyphenyl)-2-(4-bromophenyl)ethanone **15**

This was prepared from 4-bromophenylacetic acid, 1,2-dimethoxybenzene and PPA.² Yield 90%. An analytical sample was prepared by recrystallisation from ethanol, mp 142–143 °C (Found: C, 60.3; H, 4.9. $\text{C}_{16}\text{H}_{15}\text{BrO}_3$ requires C, 60.0; H, 4.7%); $\nu_{\text{max}}(\text{mull})/\text{cm}^{-1}$: 1675 (C=O); δ_{H} : 3.85, 3.90 (6H, s, OCH_3), 4.15 (2H, s, CH_2), 7.02 (3H, m, Ar), 7.50 (4H, m, Ar).

N-[1-(3,4-Dimethoxyphenyl)-2-(4-bromophenyl)ethyl]formamide **1**

This was prepared from ketone **15** and formamide.² Yield 80%. An analytical sample was prepared by recrystallisation from ethanol, mp 154–155 °C (Found: C, 56.7; H, 5.3; N, 3.9. $\text{C}_{17}\text{H}_{18}\text{BrNO}_3$ requires C, 56.3; H, 5.0; N 3.8%); $\nu_{\text{max}}(\text{mull})/\text{cm}^{-1}$: 3350 (NH), 1670 (C=O); δ_{H} : 3.65 (2H, d, $J_{1,2}$ 7.2, CH_2), 3.79, 3.84 (6H, s, OCH_3), 5.22 (1H, m, CH), 6.04 (1H, br s, NH), 6.70 (2H, d, Ar), 6.77 (1H, s, Ar), 6.91 (2H, d, Ar), 7.35 (2H, d, Ar), 8.12 (1H, s, CHO).

N-[1-(3,4-Dimethoxyphenyl)-2-(4-bromophenyl)ethyl]acetamide **2**

This was prepared from amide **1**.² Yield 77%. An analytical sample was prepared by recrystallisation from ethanol, mp 169–170 °C (Found: C, 56.9; H, 5.6; N, 3.8. $\text{C}_{18}\text{H}_{20}\text{BrNO}_3$ requires C, 57.2; H, 5.3; N 3.7%); $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$: 3400 (NH), 1675 (C=O); δ_{H} : 1.93 (3H, s, CH_3), 3.00 (2H, m, CH_2), 3.78, 3.83 (6H, s, OCH_3), 5.10 (1H, m, CH), 6.00 (br s, 1H, br s, NH), 6.70 (2H, d, Ar), 6.77 (1H, s, Ar), 6.91 (2H, d, Ar), 7.35 (2H, d, Ar).

General procedure for the cyclodimerisation reaction with EPP²

A solution of amide or stilbene (1 mmol) and EPP (2.56 g) in chloroform–ether was warmed at 80 °C for 8 h. After removing the solvent *in vacuo*, water and methylene chloride were added to the crude product. The organic layer was separated, and

washed with aqueous NaOH (5%) and water. The organic extract was dried over MgSO₄ and the solvent was removed *in vacuo*. Chromatography of the crude product on an alumina column (eluent benzene–hexane) afforded stilbenes and the cyclodimer mixtures. The mixture of cyclodimers was separated by PTLC or recrystallisation. The stilbenes **8** and **9** have been previously described.¹⁶

Cyclodimers obtained from amides **1** and **2**

These amides rendered stilbene **7** (25 and 26% respectively from **1** and **2**) and a mixture of cyclodimers **7-I** and **7-II** (53 and 67% respectively). The compounds **7-I** and **7-II** were obtained as a mixture. This mixture was heated at reflux with ethanol. The insoluble phase was filtered off while hot and it was identified as **7-I**. Mp 184–185 °C (ethanol). The mother liquors were cooled and a second product identified as **7-II** appeared. It was filtered and dried. Mp 165–166 °C (ethanol).

trans-1,2-Dimethoxy-4-[2-(4-bromophenyl)ethenyl]benzene 7. Mp 120–121 °C (ethanol) (Found: C, 60.8; H, 4.6. C₁₆H₁₅BrO₃ requires C, 60.3; H, 4.7%); ν_{\max} (neat)/cm⁻¹: 980 (HC=CH); δ_{H} : 3.75, 3.85 (6H, s, OCH₃), 6.90 (5H, m, Ar and HC=CH), 7.25 (2H, d, Ar-2,6), 7.40 (2H, d, Ar-3,5).

r-1-(4-Bromobenzyl)-c-2-(4-bromophenyl)-t-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane 7-I. Mp 184–185 °C (ethanol). δ_{H} : 2.31 (1H, dd, J_{gem} 13.3, $J_{\text{CH}_2\text{-H-1}}$ 10.8, CH₂Ph), 2.46 (1H, dd, J_{gem} 13.3, $J_{\text{CH}_2\text{-H-1}}$ 5.4, CH₂Ph), 3.54 (1H, m, H-1), 3.87 (1H, m, H-2), 3.60, 3.74, 3.76, 3.83 (12H, s, OCH₃), 4.62 (1H, d, $J_{2,3}$ 9.8, H-3), 5.92 (1H, s, Ar), 6.46 (1H, s, Ar), 6.70 (4H, m, Ar), 7.29 (7H, m, Ar). The aliphatic hydrogens were assigned by decoupling experiments. δ_{C} : 36.7, 49.9, 52.8, 55.5, 55.6, 55.7, 55.9, 59.6, 107.7, 108.0, 111.1, 111.2, 119.5, 120.1, 120.6, 130.3, 130.7, 131.2, 135.2, 136.3, 136.8, 138.8, 139.1, 147.5, 147.8, 148.6, 148.9; m/z : 640, 638, 636 (M⁺, 7.5, 13.8, 7.3%), 469 (100), 467 (98.9), 388 (10.5), 331 (10.2), 329 (10.5), 171 (2.8), 169 (3.1), 151 (10.6).

r-1-(4-Bromobenzyl)-t-2-(4-bromophenyl)-c-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane 7-II. Mp 165–166 °C (ethanol). δ_{H} : 2.92 (2H, m, CH₂Ph), 3.01 (1H, m, H-2), 3.69, 3.74, 3.80, 3.84 (12H, s, OCH₃), 3.85 (1H, m, H-1), 4.14 (1H, d, $J_{2,3}$ 9.2, H-3), 6.86 (13H, m, Ar). The aliphatic hydrogens were assigned by decoupling experiments. δ_{C} : 39.9, 51.5, 55.7, 55.9, 59.1, 62.6, 106.9, 107.9, 110.9, 119.9, 120.0, 120.4, 129.6, 131.1, 131.3, 135.8, 136.3, 136.4, 138.4, 141.5, 147.7, 148.6, 148.9; m/z : 640, 638, 636 (M⁺, 1.5, 3.4, 3.6%), 469 (95.5), 467 (100), 388 (10.7), 331 (18.0), 329 (17.0), 171 (33.9), 169 (37.1), 151 (19.7).

Cyclodimer obtained from amides **3** and **4**

r-1,t-2,c-3-Tris(3,4-dimethoxyphenyl)-6,7-dimethoxytetralin 8-I. This compound was obtained by treatment of amides **3** and **4** with EPP as the unique product. From both amides the yield was 99%. Mp 153–156 °C (methanol). δ_{H} : 3.05 (1H, dd, $J_{1,2}$ 10.3, $J_{2,3}$ 11.5, H-2), 3.06 (1H, dd, $J_{3,4b}$ 11.5, $J_{4a,4b}$ 15.7, H-4b), 3.21 (1H, dd, $J_{3,4a}$ 4.1, $J_{4a,4b}$ 15.7, H-4a), 3.36 (1H, m, $J_{2,3}$ 11.5, $J_{3,4a}$ 4.1, $J_{3,4b}$ 11.5, H-3), 4.16 (1H, d, $J_{1,2}$ 10.3, H-1), 6.45 (1H, m, Ar); δ_{C} : 38.9, 45.8, 54.1, 54.8, 54.9, 55.0, 55.4, 109.8, 109.9, 110.1, 110.5, 111.1, 111.9, 118.9, 120.1, 120.6, 128.3, 130.7, 134.8, 136.3, 137.2, 146.5, 146.6, 147.4, 147.5, 147.8; m/z : 600 (M⁺, 9.3%), 449 (10.1), 300 (48.0), 285 (16.5), 270 (32.1), 269 (100), 239 (7.2), 238 (20.1), 225 (9.4), 211 (7.0), 195 (5.2), 165 (6.3), 151 (22.6).

Cyclodimers obtained from amides **5** and **6**

The amide **5** gave, by treatment with EPP, the stilbene **9** (20%) and the mixture of CDs **9-I**, **9-II** and **9-III** (45%). The compounds **9-I** and **9-III** were separated by PTLC with benzene as eluent. The compound **9-II** was obtained as a mixture with

9-III. The upper band yielded **9-I**, the middle band gave the mixture of **9-II** and **9-III** and the lower band gave **9-III**.

r-1-Benzyl-c-2-phenyl-t-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane 9-I. This compound was isolated as an oil. δ_{H} : 2.5 (2H, m, CH₂Ph), 3.50 (1H, m, H-1), 3.82 (1H, m, H-2), 3.52, 3.71, 3.76, 3.85 (12H, s, OCH₃), 4.73 (1H, d, $J_{2,3}$ 9.6, H-3), 5.85 (1H, s, Ar), 6.8 (14H, m, Ar); δ_{C} : 37.5, 50.5, 52.7, 55.4, 55.7, 60.5, 110.9, 111.3, 111.4, 120.7, 125.5, 126.4, 127.8, 128.2, 128.7, 129.8, 135.8, 137.0, 137.2, 140.1, 140.5, 147.1, 147.3, 148.4, 148.9; m/z : 480 (M⁺ 17.1%), 390 (29.0), 389 (100), 252 (10.2), 251 (40.3), 209 (39.1), 165 (18.0), 151 (28.4), 91 (53.3).

r-1-(3,4-Dimethoxyphenyl)-t-2,c-3-diphenyl-6,7-dimethoxytetralin 9-III. This compound was isolated as an oil. δ_{H} : 3.3 (4H, m, H-2, H-3, H-4), 3.58, 3.72, 3.73, 3.78 (12H, s, OCH₃), 4.29 (1H, d, $J_{1,2}$ 9.6, H-1), 6.75 (15H, m, Ar); δ_{C} : 39.9, 46.2, 54.9, 55.4, 55.9, 56.9, 56.9, 110.5, 110.6, 111.0, 111.6, 119.6, 121.1, 125.6, 125.8, 125.9, 127.7, 128.0, 128.1, 128.2, 128.4, 129.9, 136.9, 137.8, 139.7, 142.8, 146.8, 146.9, 148.0, 148.3.

r-1-Benzyl-t-2-phenyl-c-3-(3,4-dimethoxyphenyl)-5,6-dimethoxyindane 9-II. This compound was obtained as an inseparable mixture with cyclodimer **9-III**. δ_{C} (mixture of cyclodimers **9-II** and **9-III**): 39.9, 46.2, 51.4, 54.9, 55.4, 55.6, 55.9, 56.9, 58.8, 63.3, 107.0, 107.7, 110.5, 110.6, 111.0, 112.7, 119.6, 120.3, 120.7, 121.1, 125.6, 125.8, 125.9, 126.3, 127.7, 128.0, 128.1, 128.2, 128.4, 128.8, 129.4, 129.7, 129.9, 136.3, 136.6, 136.8, 136.9, 137.2, 137.8, 139.7, 140.0, 142.8, 146.8, 146.9, 147.4, 148.0, 148.3.

The amide **6**, by treatment with EPP, gave the stilbene **9** (30%) and the mixture of CDs **9-I**, **9-II** and **9-III** (48%). The compounds were separated as was previously described.

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