^{1}H NMR and UV–Vis spectroscopy of chlorine substituted stilbenes: conformational studies

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Abstract

^{1}H NMR and UV–Vis spectroscopic studies as well as molecular mechanics calculations have been performed for the *trans* and *cis* isomers of a series of chlorine substituted stilbenes (**2**–**10**). Correlations are found between the predicted molecular conformations and various NMR and UV–Vis spectroscopic parameters, indicating that these are suitable for conformational studies. The ethylene proton chemical shifts, in particular, are found to be sensitive to anisotropy effects of the nearby C–Cl bonds. Both ethylene and some ring proton chemical shifts are found to be dependent on the ring current effects, which are substituent and ring orientation dependent. UV spectra support the structural predictions based on the molecular mechanic vs. NMR correlation analysis. Average minimum energy conformations of compounds **1**–**10** are given in the paper. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Stilbene is one of the most thoroughly studied compound from the standpoint of mechanistic and preparative photochemistry [1–4]. Early photochemical studies emphasized derivation of standard photochemical parameters for the *cis*–*trans* photoisomerization processes, such as photostationary state (pss) and quantum yield (ϕ) values [1]. The importance of the ring closure reaction channel in *cis*-stilbene was recognized early [5] and most recently stilbene has become a prototype for ultrafast studies of photoisomerization [4,6-9]. Despite the importance of stilbene photochemistry analogous studies have been performed for only a limited range of stilbene derivatives.

Our ultimate goal is to obtain a clearer picture of the effect of substituents and solvents on photoisomerization processes for stilbene derivatives. In previous publications we have presented standard photoisomerization studies of methyl α-arylcinnamates using laser photolysis techniques [10,11]. In the near future photochemical studies of ring halogenated stilbenes as well as α-arylcinnamates will be presented [12,13].

The extensive studies on the unsubstituted stilbenes have revealed the importance of the nature of the ground state in the photochemical processes involved. Hence a systematic and thorough study of the photochemistry of its derivatives requires analysis of the

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trans   **cis**

ring(1)   ring (2)   ring (1)   ring(2)
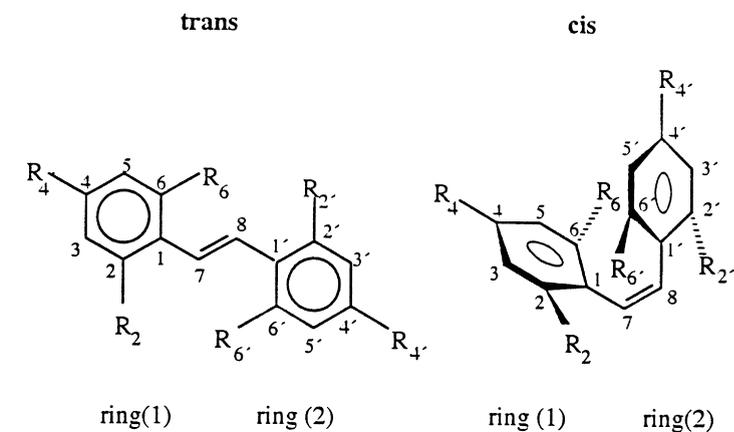
Compound	Cl positions Ring(1)/ring(2)	R_2	R_4	R_6	$R_{2'}$	$R_{4'}$	$R_{6'}$
1	-- / --	H	H	H	H	H	H
2	-- / 4′	H	H	H	H	Cl	H
3	4 / 4′	H	Cl	H	H	Cl	H
4	-- / 2′4′	H	H	H	Cl	Cl	H
5	4 / 2′4′	H	Cl	H	Cl	Cl	H
6	24 / 2′4′	Cl	Cl	H	Cl	Cl	H
7	-- / 2′6′	H	H	H	Cl	H	Cl
8	4 / 2′6′	H	Cl	H	Cl	H	Cl
9	24 / 2′6′	Cl	Cl	H	Cl	H	Cl
10	26 / 2′6′	Cl	H	Cl	Cl	H	Cl

Scheme 1.

ground states as well as the excited states and the photochemical processes involved. Determination of ground state stilbene geometries has been made both experimentally [14] and by calculations [11,15], mainly independently [11,14] but to a less extend by correlation analysis of calculation and experimental data [15].

In this paper we present data and interpretations relevant to the ground states for both *trans* and *cis* isomers of compounds **1–10** (see Scheme 1). The analysis method emphasizes the effects of chlorine substituents on conformational changes. We make use of ^{1}H NMR spectra analysis coupled with molecular mechanics calculations and UV–Vis spectra in order to find a correlation between the NMR parameters and molecular geometry. This method has

been emphasized within our department for different systems for some time [16].

2. Experimental

2.1. Chemicals

The *trans*-stilbene derivatives were prepared by the Wadsworth–Emmons modification of the Wittig reaction from appropriately substituted chloroderivatives of dimethyl benzylphosphonate and benzaldehyde [17]. For the preparation of the *cis* isomers, we made use of the fact that the photostationary state mixtures of the stilbenes favored in all cases the *cis* isomer [18]. Accordingly, the *cis* isomers are

Table 1

Minimum energy geometries of stilbenes: Dihedral angles $\theta_{(1)}$ (C_6–C_1–C_7–C_8) and $\theta_{(2)}$ (C_7–C_8–$C_{1'}$–$C_{6'}$) (see Scheme 1) calculated by MM3 for *trans/cis* conformations of compounds **1**–**10**

Compound	Cl positions ring(1)/ring(2)	$\theta_{(1)}$ *trans/cis*	$\theta_{(2)}$ *trans/cis*	(1)/(2) Basic geometries for *trans* stilbenes
1	–/–	0/39	0/39	flat/flat
2	–/-4′	0/39	0/39	flat/flat
3	-4/-4′	0/39	0/39	flat/flat
4	–/2′4′	0/38	0/43	flat/flat
5	-4/2′4′	0/39	0/46	flat/flat
6	24/2′4′	0/38	0/59	flat/flat
7	–/2′6′	4/33	56/62	flat/tilted
8	-4/2′6′	4/33	56/62	flat/tilted
9	24/2′6′	24/60	57/59	[flat-tilted]/tilted
10	26/2′6′	56/ 59	55/59	tilted/tilted

conveniently obtained by irradiating a *n*-hexane solution of the *trans* isomer and separated from the resulting mixture of *cis* and *trans* isomers by chromatography.

2.2. ^1H NMR

Spectra were run on a Bruker AC 250 MHz spectrometer for all compounds dissolved in $CDCl_3$. Chemical shifts were found relative to TMS. Proton signals were assigned by means of decoupling and COSY techniques and nuclear chemical shifts and coupling constants were derived by spectra simulations using the software package, LAOCOON [19].

2.3. UV–Vis spectra

UV–Visible absorption spectra were measured for all compounds dissolved in *n*-hexane using Perkin–Elmer 124, Double Beam spectrophotometer. Data was transferred to a Macintosh computer for manipulation and displaying, using the IGOR Pro 3.0 software package (WaveMetrics).

3. Results and interpretations

3.1. Molecular mechanics calculations

Molecular mechanics calculations were performed on Macintosh computers using both the MM2(91) and MM3(92) software packages in conjunction with MacMimic from Instar Software.

Bond distances and angles were determined for the minimum energy conformations, using MM3 and MM2. Good qualitative agreement was found between the two methods for all compounds except for the *trans* isomer of **6**, which molecular structure is predicted to be flat by MM3, but nonplanar by MM2. In Table 1, the dihedral angles $\theta_{(1)}$ defined as C_6–C_1–C_7–C_8 (i.e. ring (1)-ethylene group) and $\theta_{(2)}$ defined as C_7–C_8–$C_{1'}$–$C_{6'}$ (i.e. ring (2)-ethylene group) (see Scheme 1) for the minimum energy conformations, for all the compounds and isomers, derived by MM3, are listed.

The planar structure of the unsubstituted *trans*-stilbene compares nicely with that predicted from IR-spectra of the compound in solutions [20]. Detailed structure derived from X-ray experiments of the solid, on the other hand, differ, which is believed to be due to disorder in the crystal. The only published experimental structural data of *cis*-stilbene obtained by the electron diffraction [21] indicates a strongly nonplanar structure in agreement with our calculations. Various ab initio calculation methods, both for the *trans* and the *cis* isomers are found to give analogous minimum energy conformations as ours [20]. No experimental studies of the conformations of the substituted compounds (**2**–**10**) in solutions are available in the literature for comparison.

Minimum energy values were obtained for all the compounds and isomers as a function of the two dihedral angles ($\theta_{(1)}$ and $\theta_{(2)}$) to obtain potential energy
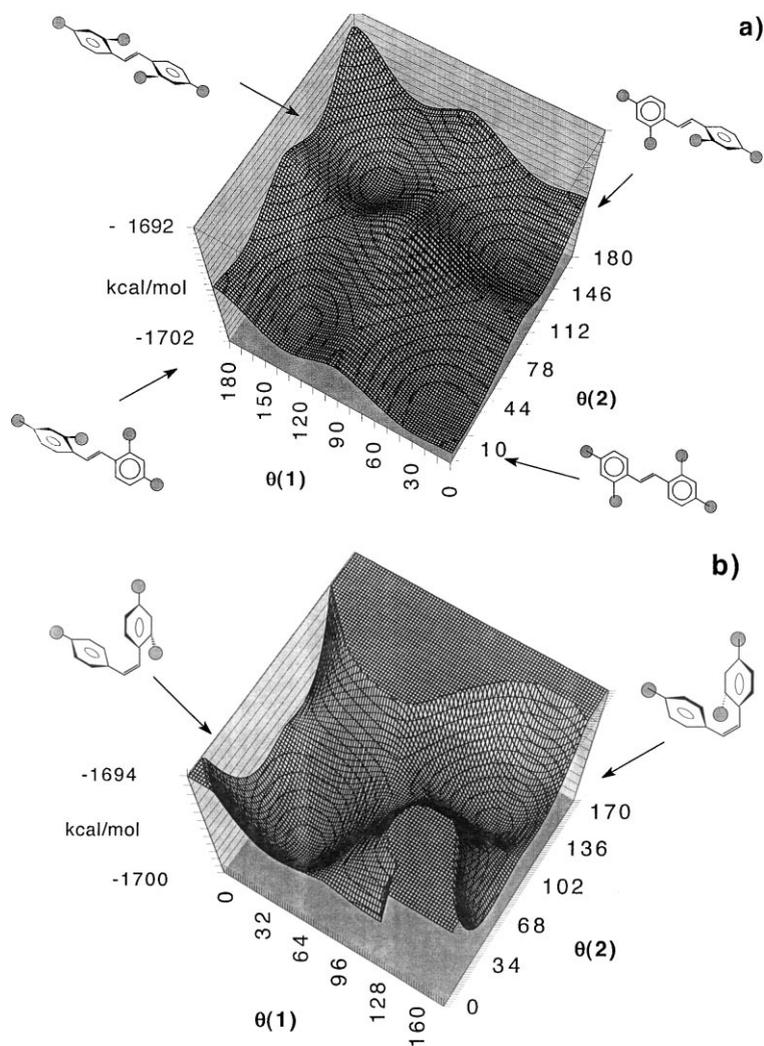
Fig. 1. Potential energy surfaces for: (a) the *trans* isomer of molecule **6**; and (b) the *cis* isomer of molecule **5**. Potential energies as functions of the dihedral angles $\theta(1)$ (C_6–C_1–C_7–C_8) and $\theta(2)$ (C_7–C_8–C_1–$C_{6'}$) (see Scheme 1). Semi-schematic molecular conformations corresponding to the potential minima are also shown.

surfaces. Fig. 1 shows two surfaces as representative examples, for the *trans* isomer of compound **6** and for the *cis* isomer of compound **5**. All the potential surfaces for the *trans* isomers show four energy minima, while those for the *cis* isomers show two. Semi-schematic figures of the corresponding molecular structures for *trans*-**6** and *cis*-**5** are also shown on Fig. 1. The dihedral angles in Table 1 correspond closely to the lowest minima on the potential surfaces. It was found to be convenient to group the compounds and

isomers according to their basic geometrical structures into three main groups: (a) compounds **1**–**6**; (b) compounds **7** and **8**; and (c) compounds **9** and **10** (see Table 1 and molecular structures on Fig. 2).

For the *trans* isomers these three groups correspond to the following.

(a) (**1**–**6**) flat molecular geometry, referred to as flat "ring(1)-ethylene group"/flat "ring(2)-ethylene group ($\theta_{(1)} = \theta_{(2)} = 0°$) (or simply flat/flat).
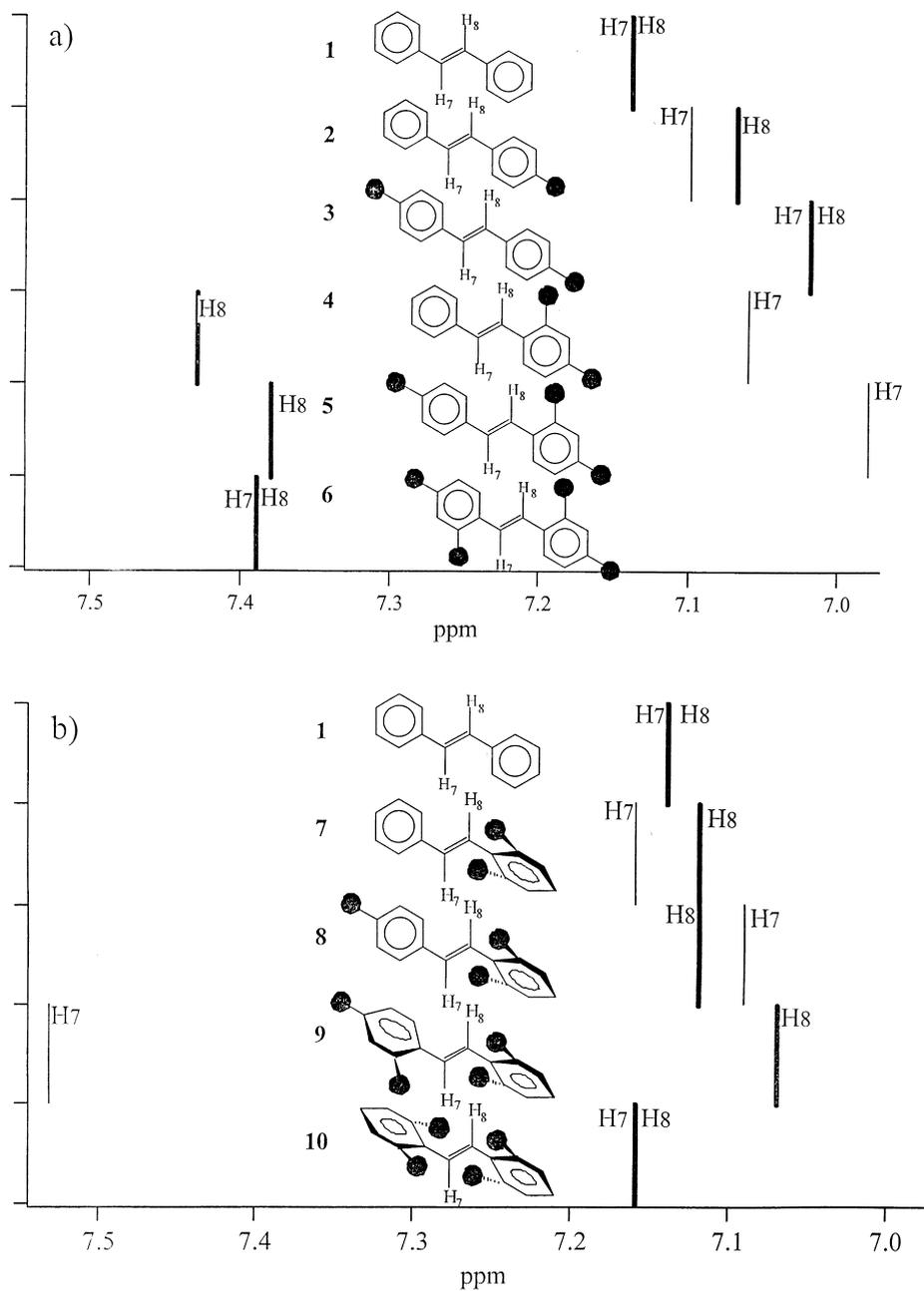
Fig. 2. Semi-schematic molecular conformations and ethylene proton chemical shifts (δ(ppm), relative to TMS) for the *trans* isomers of compounds: (a) **1–6**; and (b) **1, 7–10**.

Table 2
^{1}H-NMR chemical shifts for ethylene protons ($\delta_{trans}/\delta_{cis}$)

Compounds	Cl positions ring(1)/ring(2)	δ (H_7)/ppm ($\delta_{trans}/\delta_{cis}$)	δ (H_8)/ppm ($\delta_{trans}/\delta_{cis}$)
1	–/–	7.14/6.61	7.14/6.61
2	–/-4′	7.10/6.62	7.07/6.52
3	-4/-4′	7.02/6.56	7.02/6.56
4	–/2′4′	7.06/6.62	7.43/6.76
5	-4/2′4′	6.98/6.63	7.38/6.67
6	24/2′4′	7.39/6.80	7.39/6.80
7	–/2′6′	7.16/6.85	7.12/6.49
8	-4/2′6′	7.09/6.53	7.12/6.82
9	24/2′6′	7.53/6.98	7.07/6.61
10	26/2′6′	7.16/6.73	7.16/6.73

Table 3
^{1}H-NMR chemical shifts for ring (1) protons ($\delta_{trans}/\delta_{cis}$)

Compounds	Cl positions ring(1)/ring(2)	δ (H_2)/ppm	δ (H_3)/ ppm	δ (H_4)/ppm	δ (H_5)/ ppm	δ (H_6)/ppm	(1)-eth/eth-(2) *trans* geometries
1	–/–	7.55/7.26	7.39/7.24	7.26/7.20	7.39/7.24	7.55/7.26	flat/flat
3	-4/-4′	7.43/7.15	7.33/7.21	–	7.33/7.21	7.43/7.15	flat/flat
5	-4/2′4′	7.45/7.07	7.34/7.18	–	7.34/7.18	7.45/7.07	flat/flat
6	24/2′4′	-	7.42/7.41	–	7.27/6.99	7.65/6.92	flat/flat
8	-4/2′6′	7.47/7.02	7.35/7.21	–	7.35/7.21	7.47/7.02	flat/tilted
9	24/2′6′	–	7.42/7.38	–	7.28/6.90	7.66/6.72	[flat-tilted]/tilted
10	26/2′6′	–	7.37/7.15	7.15/7.02	7.37/7.15	–	tilted/tilted

(b) (**7,8**) flat "ring(1)-ethylene group" ($\theta_{(1)} \sim 0°$) but tilted ring 2 (i.e. nonplanar "ring(2)-ethylene group" geometry) ($\theta_{(2)} = 56°$) (flat/tilted).
(c) (**9,10**) tilted ring(1) ($\theta_{(1)} = 24°$(**9**), $56°$(**10**)) as well as ring(2) ($\theta_{(2)} = 57°$(**9**), $55°$(**10**)) (tilted/tilted). See Table 1 and Fig. 2.

All the *cis* isomers are predicted to be nonplanar (see Table 1).

(a) (**1–6**): rings (1) and (2) are tilted by about the same amount ($\theta_{(1)} = 38°–39°$), while rings (2) are tilted by $39°–59°$.
(b) (**7,8**): show slightly less tilting of rings (1) ($\theta_{(1)} = 33°$) but the largest tilting of rings (2) ($\theta_{(2)} = 62°$).
(c) (**9,10**): show large but about equal tilting of both rings ($\theta_{(1)} = \theta_{(2)} \sim 59°–60°$).

3.2. ^{1}H NMR chemical shifts

^{1}H NMR chemical shift values relative to TMS

Table 4
^{1}H-NMR chemical shifts for ring (2) protons ($\delta_{trans}/\delta_{cis}$) (see values in Table 3 for the symmetric compounds **1**, **3**, **6** and **10**)

Compounds	Cl positions ring(1)/ring(2)	δ (H_2)/ppm	δ (H_3)/ ppm	δ (H_4)/ppm	δ (H_5)/ ppm	δ (H_6)/ppm	(1)-eth/eth-(2) *trans* geometries
2	–/-4′	7.45/?	7.35/?	–	7.35/?	7.45/?	flat/flat
4	–/2′4′	–	7.40/7.44	–	7.25/7.03	7.62/7.13	flat/flat
5	-4/2′4′	–	7.40/7.43	–	7.24/7.04	7.58/7.08	flat/flat
7	-/2′6′	–	7.35/7.34	7.11/7.19	7.35/7.34	–	flat/tilted
8	-4/2′6′	–	7.35/7.38	7.12/7.24	7.35/7.38	–	flat/tilted
9	24/2′6′	–	7.36/7.27	7.14/7.14	7.36/7.27	–	[flat-tilted]/tilted

derived for the *trans* and the *cis* isomers of compounds **1**–**10** are listed in Tables 2–4.

The main trends in the ^{1}H NMR chemical shifts will now be discussed and interpreted. We will emphasize trends in chemical shifts of protons on equivalently substituted rings as the composition of the adjacent rings varies. Also we will make comparison with the corresponding values for the unsubstituted rings. Both electron acceptor/donor effects of the chlorine atoms and through space anisotropy need to be considered. In terms of the acceptor/donor effects both (i) the inductive effects which operate in the σ frame and (ii) the conjugative effects, which operate in the π-system, are of importance. In terms of through space anisotropy effects both (iii) the magnetic anisotropy of neighboring bonds and (iv) the ring current effects need to be considered [22,23].

3.3. Ethylene protons

In all cases the ethylene protons undergo upfield shift by going from the *trans* to the *cis* isomers (Table 2, $\Delta(trans–cis) = 0.3$–0.7 ppm). In terms of the unsubstituted stilbenes, this has been attributed to coplanarity of the aromatic rings for the *trans* isomer (hence a maximum high frequency *ring current shift*) but tilting of the rings for the *cis* isomer (hence less *ring current shift*) [22]. We believe that the analogous trend in the chlorine-substituted compounds (**1**–**10**) can at least partly be attributed to different ring current shifts due to predicted differences in coplanarity of the two isomers (Table 1).

A striking effect, clearly shown in Fig. 2, is a large downfield shift of one or both of the ethylene protons (H_7, H_8) in those *trans*-stilbenes that have at least one 2,4-dichlorinated ring (H_8 in **4**–**6** and H_7 in **6** and **9**). Thus $\delta(H_8) = 7.43$ ppm for **4**, $\delta(H_8) = 7.38$ ppm for **5**, $\delta(H_8) = \delta(H_7) = 7.39$ ppm for **6** and $\delta(H_7) = 7.53$ ppm for **9**, compared with values of $\delta(H_8)$ and $\delta(H_7)$ between 6.98–7.16 ppm for the other *trans*-stilbenes. These are all compounds where the "2,4-dichlorinated ring-ethylene" systems are predicted to be either flat or slightly tilted. Thus, for example, for compound **4**, this means that the C_8–H bond is close to being parallel to the $C_{2'}$–Cl, indicating that the deshielding effect is associated with the *magnetic anisotropy* of the $C_{2'}$–Cl bond, which should

be large for "flat" geometry [22]. More generally, the protons that undergo large downfield shifts are those shown in Fig. 2 in close proximity to the 2,4-dichlorinated rings with the C–H bonds (close to being) parallel to the C_2–Cl ($C_{2'}$–Cl) bonds. A lesser but significant effect of the analogous type is observed for the *cis* isomers with 2,4-dichlorinated rings (H_8 in **4** and **5** and H_7 in **9**) (see Table 2). Thus, the H_8 protons are shifted downfield relative to the *cis*-stilbene ethylene protons ($\delta = 6.61$ ppm) and the H_7 protons for compounds **4** ($\delta(H_8) = 6.76$ ppm; $\delta(H_7) = 6.62$ ppm) and **5** (($\delta H_8) = 6.67$ ppm; $\delta(H_7) = 6.63$ ppm). The H_7 proton for **9** is also shifted downfield ($\delta(H_7) = 6.98$ ppm; $\delta(H_8) = 6.61$ ppm). An analogous effect, on the other hand, is not seen for the corresponding ethylene protons closest to the 2,6-dichlorinated rings, for the *trans* isomers (thus, $\delta(H_8) = 7.12$ ppm for **7**, $\delta(H_8) = 7.12$ ppm for **8**, $\delta(H_8) = 7.07$ ppm for **9** and $\delta(H_8) = 7.16$ ppm for **10**). These are predicted to be more tilted. This suggests that the deshielding effect due to magnetic anisotropy of the $C_{2'}$–Cl (C_2–Cl) bonds is less for the 2,6-dichlorinated rings, due to the nonplanarity. In summary all these findings can be understood as being largely due to the *magnetic anisotropy* effects of the C_2–Cl ($C_{2'}$–Cl) bond, with decreasing deshielding effects with distance from the corresponding ring plane, as well as with the distance from the bond axis [22].

The ethylene protons are found to undergo small, but significant upfield shifts, gradually increasing with the number of chlorine substituents in positions 2 and 4 for those *trans*-stilbenes, which are predicted to have "flat" geometry (see Fig. 2a). Thus $\delta(H_7) = 7.14$ ppm (for **1**) $> \delta(H_7) = 7.10$ ppm (for **2**) $> \delta(H_7) = 7.06$ ppm (for **4**). Further $\delta(H_8) = 7.07$ ppm (for **2**) $> \delta(H_8) = 7.02$ ppm (for **3**) $> \delta(H_7) = 6.98$ ppm (for **5**). This we associate with the combined effects of decreasing ring current (iv; see above) and decreasing magnetic anisotropy (deshielding) effects of the neighboring C=C bond(s) on the phenyl rings (iii) as the electron withdrawing chlorines are added to the rings (i). Analogous effects for the "out of plane" ethylene-ring systems, other than the *cis* isomers with 2,4 chlorinated rings mentioned before (i.e. *trans* isomers of compounds **7**–**10** and *cis* isomers of compounds **1**–**3,7,8,10**) are insignificant.
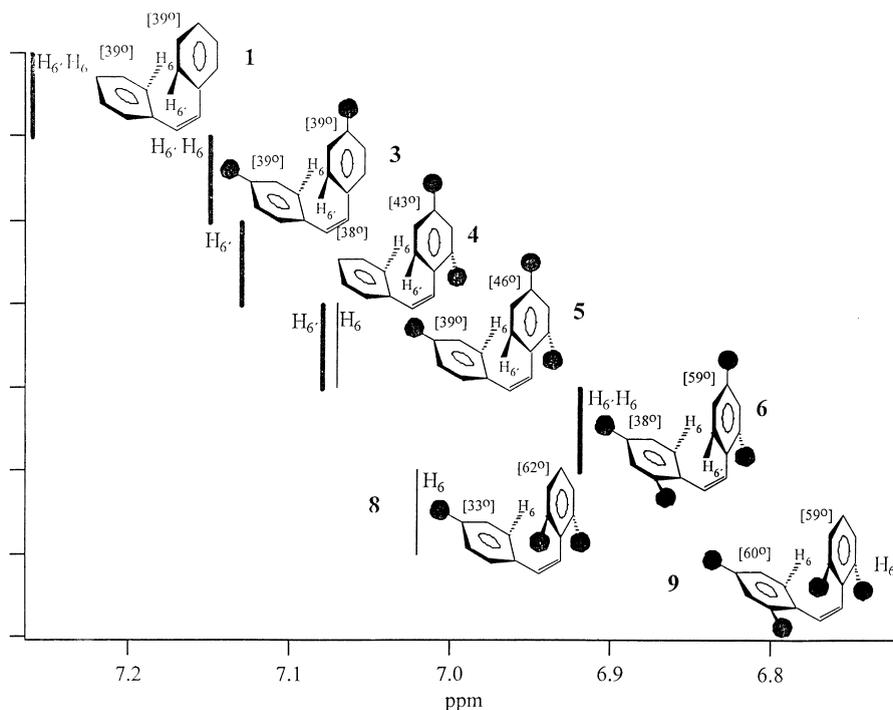
Fig. 3. Semi-schematic molecular conformations and protons 6 and 6′(see Scheme 1) chemical shifts (δ (ppm), relative to TMS) for the *cis* isomers of compounds **1**, **3–6** and **8–9**.

3.4. Ring protons

No clear trends are observed in the chemical shifts of the ring protons as the number and positions of chlorine atoms are altered for the substituted *trans*-stilbenes. This suggests that geometrical alterations do not play an important role in determining chemical shifts of the ring protons for these isomers. Most proton shifts observed, as an effect of substitutions (seen by the comparison of the substituted compounds with the unsubstituted *trans* isomer), are found to be upfield. Thus, upfield shifts of about 0.1 ppm are observed for the protons in positions 2(2′) and 6(6′), meta to chlorine atoms in positions 4 (4′) ($\delta(H_2) = 7.55$ ppm for **1** vs $\delta(H_2) = 7.45$ ppm for **2**, $\delta(H_2) = 7.43$ ppm for **3**, $\delta(H_2) = 7.45$ ppm for **5** and $\delta(H_2) = 7.47$ ppm for **8**; see columns 2 in Tables 3 and 4). This can be compared with a 0.11 ppm shift of the *meta* protons in chlorobenzene ($\delta(C_6H_5Cl) = 7.225$ ppm vs $\delta(C_6H_6) = 7.339$ ppm [24,25]). Upfield shifts of about 0.11–0.15 ppm are observed for the protons in positions 4 (4′), *meta* to two chlorine atoms in

positions 2 and 6 (2′ and 6′) ($\delta(H_4) = 7.26$ ppm for **1** vs $\delta(H_4) = 7.11$ ppm for **7**, $\delta(H_4) = 7.12$ ppm for **8**, $\delta(H_4) = 7.14$ ppm for **9** and $\delta(H_4) = 7.15$ ppm for **10**; see columns 4 in Tables 3 and 4). This can be compared with a 0.29 ppm shift of the *meta* proton in *m*-dichlorobenzene ($\delta(C_6H_4Cl_2) = 7.051$ ppm vs $\delta(C_6H_6) = 7.339$ ppm [24,26]). Furthermore, upfield shifts of about 0.11–0.15 ppm are observed for the $H_5(H_{5'})$ protons for two chlorine substitutions in positions 2 and 4 (2′, 4′) ($\delta(H_5) = 7.39$ ppm for **1** vs $\delta(H_5) = 7.25$ ppm for **4**, $\delta(H_5) = 7.24$ ppm for **5**, $\delta(H_5) = 7.27$ ppm for **6** and $\delta(H_5) = 7.28$ ppm for **9**; see columns 5 in Tables 3 and 4). This can be compared with a 0.235 ppm shift of a proton in a corresponding position in *m*-dichlorobenzene ($\delta(C_6H_4Cl_2) = 7.104$ ppm vs $\delta(C_6H_6) = 7.339$ ppm [24,26]). These upfield shifts can be understood as being largely due to reduced *ring current* because of *inductive effects* on the substituted ring itself.

For the *cis*-stilbenes upfield shifts of the H_6 ($H_{6'}$) protons are observed as the number of chlorine atoms increases and changes in position on the

Table 5
Proton coupling constants (Hz). Empty entrances in the table are either due to nonexisting couplings or because accurate values could not be determined by the simulation procedure. Virtual couplings, needed in the simulations, are not listed. J_{trans}/J_{cis}

Compounds	Cl positions ring(1)/ring(2)	$J_{7,8}$	$J_{5,6}$	$J_{5',6'}$	$J_{3,5}$	$J_{3',5'}$	$J_{4,5}$	$J_{4',5'}$
1	–/–		7.84/7.90	7.84/7.90			7.40/7.44	7.40/7.44
2	–/-4′	16.64/12.22		8.47/ -				
3	-4/-4′		8.54/8.50	8.54/8.50				
4	–/2′4′	16.29/12.14		8.50/8.30		2.15/2.08		
5	-4/2′4′	16.29/12.14	8.38/8.50	8.50/8.39		2.12/1.80		
6	24/2′4′		8.43/8.39	8.43/8.39	2.11/2.13	2.11/2.13		
7	–/2′6′	16.67/12.12						-/8.19
8	-4/2′6′	16.55/12.10	8.36/8.42					8.13/8.09
9	24/2′6′	16.06/11.95	8.48/8.34		2.12/2.08			8.17/8.22
10	26/2′6′						8.11/8.14	8.11/8.14

adjacent ring only (see Fig. 3). Shifts of protons in position 6 on 2,4-disubstituted rings decrease as the composition of the adjacent ring varies from non-substituted (**4**) to monosubstituted in position 4 (**5**) to doubly substituted in positions 2 and 4 (**6**) to doubly substituted in positions 2 and 6 (**9**) ($\{\delta(H_{6'}) = 7.13$ ppm (**4**)$\} > \{\delta(H_{6'}) = 7.08$ ppm (**5**)$\} > \{\delta(H_{6'}) = \delta(H_6) = 6.92$ ppm (**6**)$\} > \{\delta(H_6) = 6.72$ ppm (**9**)$\}$). Similarly the chemical shifts of protons in positions 6 on 4 substituted rings decrease slightly, but significantly as the composition of the adjacent ring varies from monosubstituted in position 4 (**3**) to doubly substituted in positions 2 and 4 (**5**) to doubly substituted in positions 2 and 6 (**8**), ($\{\delta(H_6) = 7.15$ ppm (**3**)$\} > \{\delta(H_6) = 7.07$ ppm (**5**)$\} > \{\delta(H_6) = 7.02$ ppm (**8**)$\}$. This can be understood as being due to a combination of geometrical alterations and *effects of substituents* on *ring currents*. The lowering in ring current as the number of chlorine substituents increases will cause upfield shifts of the H_6 protons on the adjacent ring. This is due to the tilting (Scheme 1 and Fig. 3) of both rings, which causes the H_6 nuclei to lie in the shielding region of the adjacent ring. This is the main reason for the shifts observed for $H_{6'}$ as **4** > **5** and for H_6 as **3** > **5**, i.e. for compounds close in geometrical structures (see Table 1 and Fig. 3). However, alterations in the geometrical structure (tilting of rings) for identical number of substituents will affect the shielding of $H_6(H_{6'})$ due to the *ring current* of the adjacent ring [22,27]. This could be the main explanation for the upfield shifts of H_6 as **6** > **9** and as **5** > **8**, which are associated with increased tilting of the rings. An upfield shift of the

$H_5(H_{5'})$ protons on the 2,4 substituted rings (H_5 on **6** and **9** and $H_{5'}$ on **4** and **5**) of the *cis* isomer relative to the unsubstituted ring is likely to be due to reduced ring currents on the substituted rings.

Other observed shifts of protons as an effect of substitution or as an effect of number or positions of substituents were not found to correlate with molecular structure changes equally straightforward as those mentioned above. Hence we believe that these are due to less isolated/more mixed combinations of effects. Among those are the following observations. (1) Downfield shifts of the $H_6(H_{6'})$ protons on the 2,4 substituted rings of the *trans* isomers (H_6 on **6** and **9** and $H_{6'}$ on **4** and **5**) relative to the unsubstituted ring (1) (see Tables 3 and 4). (2) Downfield shifts of the $H_3(H_{3'})$ protons on the 2,4 and 2,6 substituted rings of the *cis* isomers (H_3 on **6** and **9** and $H_{3'}$ on **4,5,7,8** and **9**) relative to H_3 on **1** (see Table 3 and 4).

3.5. ^1H NMR coupling constants

^1H NMR coupling constants derived for the *trans* and *cis* isomers of compounds **1**–**10** are listed in Table 5. The main characteristics of the data will now be discussed.

Firstly a lowering in the coupling between the ethylene protons from the *trans* (16.06–16.67 Hz) to the *cis* (11.95–12.22 Hz) isomers, is clearly observed. This is in agreement with general observations for vicinal couplings in alkenes, predicted by the valence bond theory as commonly expressed by the Karplus equation [22,23]. Secondly an increase in the ring

Table 6
Wavelengths and wavenumbers of peak maxima in UV spectra (λ_{max}, ν_{max}) of the stilbenes (*trans/cis*). Compounds with observed vibrational structure in the wavelength range 250–350 nm are specifically marked

Compound	Cl positions ring(1)/ring(2)	λ_{max}/nm *trans/cis*	ν_{max}/cm^{-1} *trans / cis*	Vibrational structure observed for *trans* isomers
1	–/–	294/276	34010/36230	X
2	–/-4′	299/280	33450/35710	X
3	-4/-4′	302/285	33110/35090	X
4	–/2′4′	300/280	33330/35710	X
5	-4/2′4′	303/284	33000/35210	X
6	24/2′4′	304/280	32900/35710	X
7	–/2′6′	288/259	34720/38610	
8	-4/2′6′	290/265	34480/37740	
9	24/2′6′	283/262	35340/38170	
10	26/2′6′	273/255	36630/39220	

vicinal coupling constants from the unsubstituted stilbene phenyl rings (7.40–7.90 Hz) to the substituted rings (8.09–8.54 Hz), is observed. This effect must be associated with the σ-*acceptor*, but weak π-*donor* nature of the chlorine substituents [23]. However, no clear effects of number (one or two) or positions (2,4 or 2,6) of chlorine substituents are observed. A small, but

significant, lowering in the ethylene proton coupling constants is observed by going from the group a and b molecules (**2,4,5,7,8**) to a group c molecule (**9**), both for the *trans* and the *cis* isomers. Most probably this is due to some distortion effects of the chlorines in positions 2 and 6, hence tilting of the rings which could affect the Karplus equation of concern.
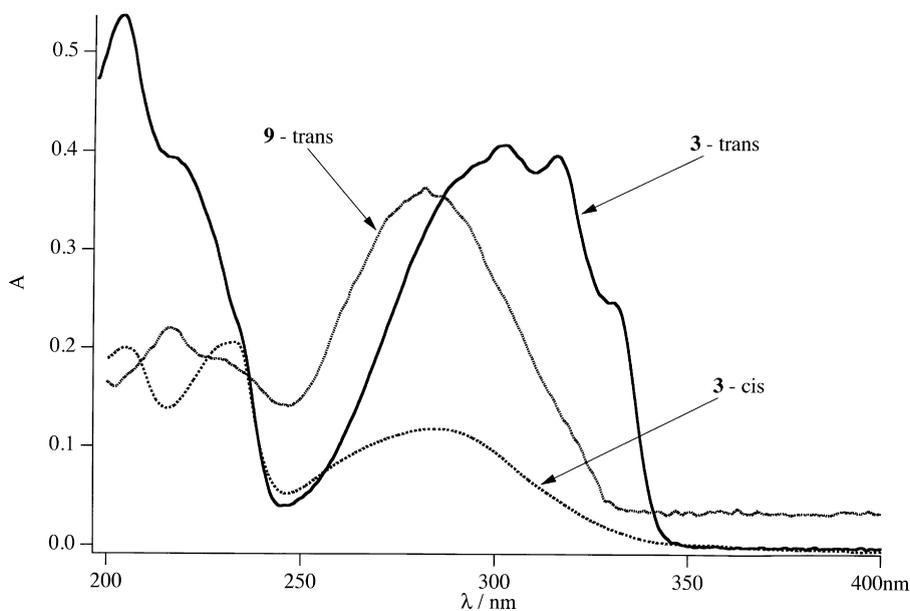

Fig. 4. UV absorption spectra of compounds **3**-*trans*, **3**-*cis* and **9**-*trans* dissolved in *n*-hexane. Vibrational structure, appearing as broad peaks or shoulders in the spectral region 250–350 nm, is found for compounds with planar geometry (such as **3**-*trans*) only. Peak maxima in this spectral region shift to shorter wavelenght as the molecular structure changes from planar(**3**-*trans*) to nonplanar (**3**-*cis* and **9**-*trans*). Spectra were recorded for 1×10^{-4} M solutions in 1 cm wide cuvettes.

3.6. UV–Vis spectroscopy

UV absorption spectra of the compounds typically show absorption below about 350 nm with a broad peak extending to about 250 nm, followed by a rapidly increasing absorption to lower wavelength. Spectra of the *trans* isomers of compounds **3** and **9** and of the *cis* isomer of compound **3** are shown in Fig. 4. Peak maxima of compounds **1**–**10** are listed in Table 6. The 250–350 nm spectra for the unsubstituted stilbenes are believed to be largely due to a $\pi \rightarrow \pi^*$ transition. The π orbital is localized in the region of the olefinic double bond to a large extent, but it is affected by conjugative effects of the phenyl rings [2,3]. *Trans*-stilbene shows a clear vibrational structure whereas *cis*-stilbene shows weaker absorption shifted slightly to shorter wavelength with no fine structure. This difference in the two spectra has been associated with structural differences of the two isomers, the *trans* isomers being planar but the *cis* isomers being twisted. In Table 6 spectra of compounds **1**–**10** with and without observed vibrational structure are specified (see also Fig. 4). According to Table 6, spectra due to the $\pi \rightarrow \pi^*$ transitions are found to shift to shorter wavelength from the *trans* to *cis* isomers for all the compounds. Vibrational structure is observed for all the *trans* isomers in group a (**1**–**6**; flat/flat geometry). It appears as broad peaks or shoulders as shown for the *trans* isomer of compound **3** in Fig. 4. Spacings between neighbor peaks are found to be in the range 1200–1600 cm^{-1}. On the other hand vibrational structure is not seen for the *trans* isomer of the groups b and c molecules (**7**–**10**; flat/tilted and tilted/tilted geometries) nor is it seen for any of the *cis* isomers (see Fig. 4). These observations further support the prediction that indeed the *trans* molecules **1**–**6** are planar, while the rest of the molecules and isomers (*trans*-**7**–**10** and all *cis* isomers) are twisted.

4. Conclusions

^{1}H NMR and UV–Vis spectra of nine chlorine substituted stilbenes (**2**–**10**) and the unsubstituted stilbenes for both the *trans* and *cis* isomers have been recorded and analyzed. Correlations between spectral data and molecular geometry information derived from force field molecular mechanics calculations were sought.

The ^{1}H NMR chemical shifts for the ethylene protons, in particular, were found to be conformation dependent. Clear differences in chemical shifts are observed for the *trans* and *cis* isomers due to differences in molecular structure planarity. Furthermore, the ethylene proton chemical shifts are found to be largely dependent on the orientation with respect to the closest C–Cl bonds, due to its anisotropy effects. Finally the shifts are found to be affected by reduced current effects due to the chlorine ring substitutions for planar molecular structures.

Most of the observed ring proton shifts of the *trans* isomers could be explained as being due to electron withdrawing effects of the substituents on the same ring, hence being independent of the molecular conformations. Ring proton chemical shifts of the *cis* isomers, on the other hand, were found to be affected by substituent dependent ring currents of the adjacent rings. This depends on the magnitude of tilting of the rings.

Observed changes in the proton couplings are mainly associated with alterations in the electron structure closest to the nuclei of concern. Hence, effects of overall alterations in molecular conformations on couplings are believed to be limited. However, there is some indication that the ethylene proton couplings are affected by large tilting due to steric hindrances of the rings.

A clear correlation is found between the planarity of the molecules and the positions of bands and the vibrational structures observed in the UV spectra of the compounds.

No discrepancy is found between the ^{1}H NMR and UV–Vis experimental data on the one hand and the molecular structure predictions made by the molecular modeling calculations. On the contrary, correlations between the various spectroscopic parameters and the molecular conformations have been found. Hence, we believe that the molecular geometries presented in the paper (see Table 1 and Figs. 2 and 3) represent average minimum energy conformations of the compounds **1**–**10**.

Acknowledgements

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