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Molecular Geometry and Electronic Structure of Chloro-substituted *Trans*- and *Cis*-Stilbene Derivatives

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Geometrical structures of several chlorostilbenes were determined from ultraviolet absorption spectra in solution by calculations based on the simple LCAO molecular orbital method. Dipole moments were evaluated for all derivatives without a center of symmetry in the calculated geometry. The results are in good agreement with experimental data.

Les structures géométriques de plusieurs chlorostilbènes ont été déterminées à partir des spectres d'absorption ultraviolette en solution par des calculs fondés sur la méthode simple des orbitales moléculaires. Pour tous les dérivés sans centre de symétrie les moments dipolaires ont été évalués à l'aide de la géométrie calculée. Les résultats sont en bon accord avec l'expérience.

Die geometrischen Strukturen einiger Chlorostilbene werden aus den UV-Absorptionsspektren in Lösung mittels einfacher MO–LCAO Berechnungen erhalten. Für alle Verbindungen, deren berechnete Struktur kein Symmetriezentrum aufweist, werden die Dipolmomente bestimmt. Die Resultate stehen in gutem Einklang mit den experimentellen Daten.

Introduction

In the course of a systematic research on the molecular geometry and on the electronic spectra of sterically hindered aromatic compounds [*10, 11, 12, 13*], several chlorostilbenes have been taken into consideration. This class of derivatives is very suitable for an extensive study as it is possible to obtain monochloro- and symmetrically or not symmetrically substituted polychloro-compounds, in their *cis* and *trans* forms, and because steric hindrance of the chlorine atom could determine a deviation from the planar structure when the halogen is in the α-position or in the *ortho*-position to a phenyl ring.

Contrarily to the previous papers, in this study the steric repulsion energy and the deformation energy of the σ-bonds were not explicitly considered; the molecular geometry was simply established through a comparison between the theoretical energy, corresponding to the transition of an electron from the highest occupied molecular orbital in the ground state to the lowest unoccupied orbital, and the frequency of maximum absorption in the corresponding experimental band.

In the derivative without a center of symmetry, once the geometrical structure was determined, the dipole moment was calculated and compared, whenever possible, with experimental data.

Table 1. *Absorption maxima in the electronic spectra of chlorostilbenes*

Compound	solvent	λ_{max} (Å)	log ε_{max}
trans-3-chlorostilbene	methanol	2950	4.53
	cyclohexane	2860	4.51
cis-2-chlorostilbene	methanol	2700[a]	4.01
	cyclohexane	2780	4.24
trans-2-chlorostilbene	methanol	2850[b]	4.57
	cyclohexane	2950	4.46
cis-α-chlorostilbene	methanol	2740	4.28
	cyclohexane	2810	3.93
trans-α-chlorostilbene	methanol	2850	4.52
	cyclohexane	2880	4.41

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[a] In 95% ethanol solution [*9*], $\lambda_{max} = 2700$ Å and log $\varepsilon_{max} = 4.05$.

[b] In 95% ethanol solution [*9*], $\lambda_{max} = 2980$ Å and log $\varepsilon_{max} = 4.42$.

Experimental

a) Compounds

Some chloroderivatives were synthezised by methods described in the literature, viz. *trans*-3-chlorostilbene [*4*], *cis*- and *trans*-2-chlorostilbenes [*8*], *cis*- and *trans*-α-chlorostilbenes [*7*].

b) Ultraviolet absorption spectra

Absorption in the wavelengths range between 2100 and 3500 Å was measured at room temperature with a Hitachi Perkin Elmer 139 UV-VIS Spectrophotometer. The compounds were examined in methanol and cyclohexane solution (Spectrograde C. ERBA solvents), in silica cells of 1 cm optical path length.

Data concerning the absorption maxima are given in Tab. 1.

c) Dipole moments

The electric dipole moments were determined in benzene solution at 25.0 ± 0.1 °C. The differences of refraction index between the solutions and the pure solvent were measured on a Pulfrich refractometer; the differences of dielectric constant were obtained with a "WTW" mod. DM 01 Dipolmeter, the sensitivity of which $\Delta\varepsilon/\varepsilon$ was of the order of 10^{-5}. The weight fraction of the solute in benzene was varied between 0.002 and 0.04, to obtain a sufficiently high value of $\Delta\varepsilon$ and, therefore, a good reproducibility. The dipole moments were evaluated by standard procedure and the results are given in Tabs. 2 and 4.

Method of Calculation and Results

The structure of *trans*-stilbene was supposed to be planar and bond lengths were determined by applying to the system of the 14 π-electrons the molecular orbital method in the Hückel's LCAO approximation with the β exchange integrals equal to β_0 (resonance integral for benzene). The C_α–$C_{\alpha'}$ and C_1–C_α bond orders (numbering system in Fig. 1) were first obtained; the corresponding overlap integrals were then calculated with the empirical formula of Muller, Pickett and Mulliken [*17*], and thereof new values of the β integrals were computed (a proportionality between exchange and overlap integrals was assumed). The calculation was repeated until consistent values for β and r were reached (C_α–$C_{\alpha'}$: $r = 1.355$ Å and $\beta = 1.069\,\beta_0$; C_1–C_α: $r = 1.448$ Å and $\beta = 0.914\,\beta_0$).

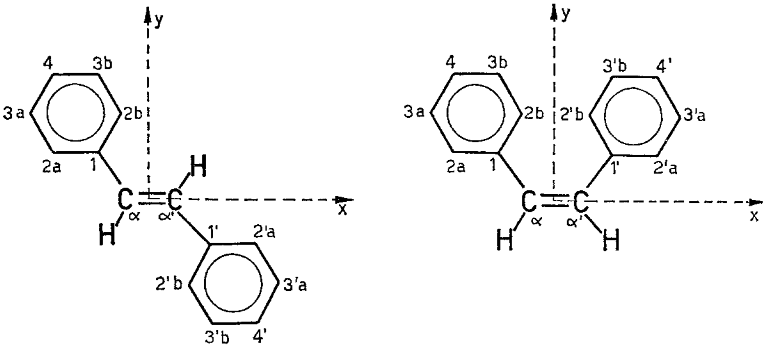

Fig. 1. Numbering system for *cis-* and *trans*-stilbene

The energy corresponding to the transition of one electron from the highest occupied molecular orbital in the ground state to the lowest unoccupied orbital was found to be 1.129 β_0; a value of 3.728 eV for β_0 was obtained from the experimental value (4.209 eV [*23*]) of the absorption maximum of the longest wavelength band.

In the case of the chloroderivatives, to obtain the energy of the molecular orbitals as a function of β_0, it is necessary to give definite values to the h_{Cl} and $k_{\mathrm{C-Cl}}$ parameters [*22*]; they were fixed so that the transition energy of the *trans*-4,4′-dichlorostilbene (experimental value: 4.09 eV [*6*]) could be exactly reproduced. A planar conformation was also supposed in this case as the particular substitution position of the chlorine atom does not cause any steric hindrance; among the possible pairs of parameter's values which satisfy the above condition, the values: $h_{\mathrm{Cl}} = 1.00$ and $k_{\mathrm{C-Cl}} = 0.34$ were selected, as they better reproduce the dipole moment of the chlorobenzene (1.58 D [*16*]). For the σ-bonds, the following values of bond moments were assumed: $\overset{+}{\mathrm{C}}\text{–}\overset{-}{\mathrm{Cl}}$: 1.57 D; $\overset{+}{\mathrm{H}}\text{–}\overset{-}{\mathrm{C}}$: 0.4 D [*20*].

The same parameters were used for the calculation of the transition energies and the dipole moments of all derivatives for which the planar structure was

Table 2. *Transition energies and dipole moments of planar chlorostilbenes*

Compound	Transition energy (eV)		Dipole moment (D)		
	obs.	theor.	obs.	theor.	φ[a]
trans-4-chlorostilbene	4.13 [*14*]	4.140	1.71 [*15*]	1.42	−28
trans-4,4′-dichlorostilbene	4.09 [*6*]	4.085	—	—	—
trans-3-chlorostilbene	4.20[b]	4.200	1.66[b]	1.59[c] 1.69[d]	−90 35.5
trans-3,3′-dichlorostilbene	[e]	4.195	—	—	—

[a] φ is the angle in degrees which the dipole moment vector makes with the y-axis (Fig. 1), positive when clockwise, negative when counter-clockwise.

[b] Present work.

[c] Chlorine atom in 3a-position.

[d] Chlorine atom in 3b-position.

[e] Not available.

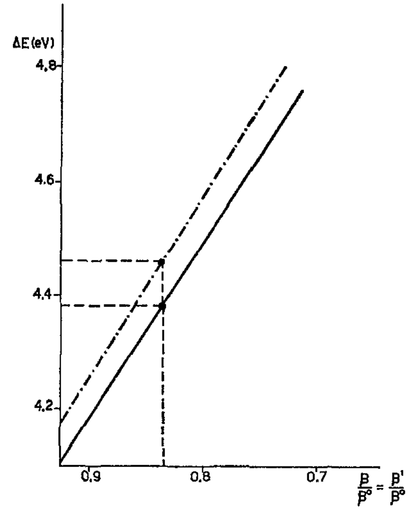

Fig. 2

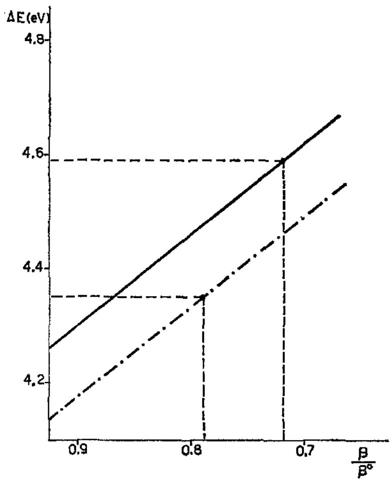

Fig. 3

Fig. 2. Dependence of the first $\pi \rightarrow \pi^*$ transition energy on β and β' exchange integrals: ——— *cis*-4-chlorostilbene; -·-·-· *cis*-stilbene

Fig. 3. Dependence of the first $\pi \rightarrow \pi^*$ transition energy on β exchange integral: ——— *cis*-2-chlorostilbene ($\beta' = 0.835\,\beta_0$); -·-·-· *trans*-2-chlorostilbene ($\beta' = 0.914\,\beta_0$)

deemed most probable; theoretical results are compared with experimental data in Tab. 2.

For *cis*-isomers and for compounds chloro-substituted in *ortho*- or α-position, the calculated energies of the first $\pi \rightarrow \pi^*$ electronic transition resulted always lower than the experimental values, when a planar conformation was considered.

Geometrical deformations due to bond-stretching were excluded because the stretching force constants are considerably higher than the bending or the twisting force constants. Among the bending and twisting deformations was considered only the rotation around the phenyl-ethylenic carbon bonds which needs of lower energy than the bending deformations and the rotation around the ethylenic bond. The dependence of the transition energy on the twisting angle of one or both the phenyl rings was examined by variation of the exchange integrals (β for the C_1–C_α bond and β' for the $C_{1'}$–$C_{\alpha'}$ bond); the resulted straight lines (ΔE vs. β or β') are given in Fig. 2—5.

It is then possible to determine the angle or the angles of rotation which are necessary to reproduce the energy of the maximum in the experimental band by the formula

$$\beta_\vartheta = \beta_{\vartheta=0} \cos\vartheta$$

justified from the assumed proportionality between exchange and overlap integrals. The results are given in Tab. 3; ϑ is the twisting angle of phenyl A and ϑ' the twisting angle of phenyl B. In the suitable conformation, the dipole moment for each chloro-compound was calculated by vector composition of π-moment and σ-bond moments; a comparison with the experimental values is made in Tab. 4.

Calculations were performed on an IBM 1620 computer.

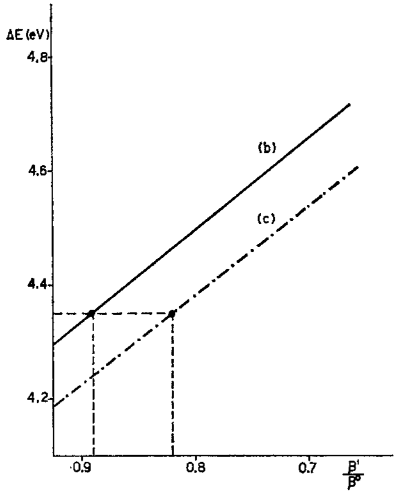

Fig. 4

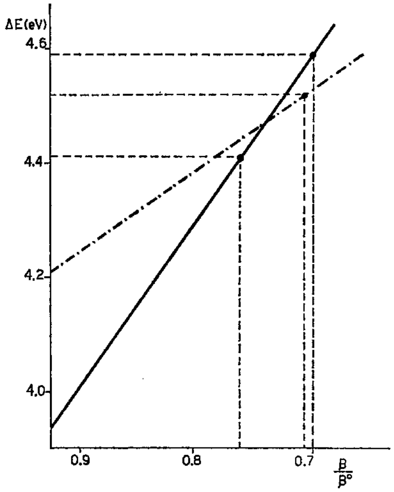

Fig. 5

Fig. 4. Dependence of the first $\pi \rightarrow \pi^*$ transition energy on β' exchange integral: ——— *trans*-α-chlorostilbene ($\beta = 0.757\ \beta_0$); -·-·-· *trans*-α-chlorostilbene ($\beta = 0.835\ \beta_0$)

Fig. 5. Dependence of the first $\pi \rightarrow \pi^*$ transition energy on β exchange integral: ——— α,α'-dichlorostilbenes (*cis* and *trans*) ($\beta = \beta'$); -·-·-· *cis*-α-chlorostilbene ($\beta' = 0.835\ \beta_0$)

Discussion

Semiempirical LCAO–SCF–CI calculations of *trans*- and *cis*-stilbene have been recently carried out and a remarkable agreement with experimental data has been achieved [*2, 5, 18*].

BEVERIDGE and JAFFÉ [*5*] have confirmed that the main transition responsible for the longest wavelength absorption on both isomers is the $^1B \leftarrow {}^1A$ transition (in the PLATT notation [*19*]); the corresponding excited state may be well represented by a simple spin-orbital configuration in which one electron is excited from the highest occupied molecular orbital in the ground state to the lowest unoccupied molecular orbital (weight of such configuration in the excited state function: 87% in the *trans*- and 80% in the *cis*-isomer [*5*]). The other excited states require a linear combination of spin-orbital configurations; excitation to these states may not be adequately described as one-electron excitation between two specific molecular orbitals and interpreted by the HMO method.

Only the energy of the longest wavelength absorption maximum is therefore compared in the present work with the theoretical predictions and the comparison can be justified especially when an empirical spectroscopic value of β_0 is adopted.

As to the parameters of the chlorine atom, it was not possible to make an empirical choice only from spectroscopic data, because the first $\pi \rightarrow \pi^*$ transition energy depends both on the coulomb integral α_{Cl} and on the exchange integral $\beta_{\mathrm{C-Cl}}$; however, the choice was possible employing the experimental value of the chlorobenzene's dipole moment, which depends considerably on the value of the coulomb integral α_{Cl} alone.

The transition energies obtained from the absorption spectra in solution for

Table 3. *Transition energies and conformations of cis-stilbene and non-planar chlorostilbenes*

Compound	transition energy (eV)	β	ϑ (°)	β'	ϑ' (°)
cis-stilbene	4.46 [*9*]	$0.835\,\beta_0$	24	$0.835\,\beta_0$	24
cis-4-chlorostilbene	4.38 [*21*]	$0.835\,\beta_0$	24	$0.835\,\beta_0$	24
trans-2-chlorostilbene	4.35[a]	$0.788\,\beta_0$	30	$0.914\,\beta_0$	0
cis-2-chlorostilbene	4.59 [*9*][a]	$0.718\,\beta_0$	38	$0.835\,\beta_0$	24
trans-α-chlorostilbene	4.35[a]	$0.757\,\beta_0$	34	$0.890\,\beta_0$	13[b]
		$0.835\,\beta_0$	24	$0.822\,\beta_0$	26[c]
cis-α-chlorostilbene	4.52[a]	$0.700\,\beta_0$	40	$0.835\,\beta_0$	24
trans-α,α'-dichlorostilbene	4.59 [*1*]	$0.694\,\beta_0$	41	$0.694\,\beta_0$	41
cis-α,α'-dichlorostilbene	4.41 [*1*]	$0.757\,\beta_0$	34	$0.757\,\beta_0$	34

[a] Present work.
[b] and [c] See Fig. 4.

the molecules with probable planar conformation (Tab. 2) were theoretically interpreted with a surprisingly good agreement in consideration of the following points: a) a simplified method of calculation was used; b) the solvent effects were not taken into consideration. Also the theoretical dipole moments agree with the experimental data and in the case of *trans*-3-chlorostilbene the conformation with the chlorine atom in 3b-position seems more probable than that with the chlorine atom in 3a-position.

For molecules which do not possess a planar conformation the twisting angles of the two phenyl rings were calculated; the value 24°, found for *cis*-stilbene,

Table 4. *Dipole moments of non-planar chlorostilbenes*

Compound	$\mu_{\text{obs.}}$ (D)	$\mu_{\text{theor.}}$ (D)	φ[a]	δ[b]
cis-4-chlorostilbene	[c]	1.60	− 28	0
trans-2-chlorostilbene	1.34[d]	1.58	−158	25
cis-2-chlorostilbene	1.56[d]	1.56[e]	−159	32.5
		2.05[f]	86	24
trans-α-chlorostilbene	1.29[d]	1.70[g]	−173	0
		1.68[h]	−163	0
cis-α-chlorostilbene	1.68[d]	1.50	−159	0
cis-α,α'-dichlorostilbene	2.69 [*3*]	2.85	180	0

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[a] φ is the angle in degrees which the projection of the dipole moment on xy plane makes with the y-axis (Fig. 1), positive when clockwise, negative when counterclockwise.
[b] δ is the angle in degrees which the dipole moment vector makes with its projection on xy plane.
[c] Not available.
[d] Present work.
[e] Chlorine atom in 2a-position.
[f] Chlorine atom in 2b-position.
[g] Case *b* in Tab. 3 and in Fig. 4.
[h] Case *c* in Tab. 3 and in Fig. 4.

confirms the previous results obtained in the interpretation of its ultraviolet spectrum [*5*, *23*]. The angle resulted on the contrary somewhat lower than that theoretically found by other criteria (43° [*11*]); however, it must be recalled that a rotation of 17° was obtained in that calculation also for the *trans*-stilbene.

The validity of the method is confirmed from the fact that the same angle of 24° resulted even in the case of *cis*-4-chlorostilbene; the deviation from the planar structure is caused by the repulsion energy of the hydrogen atoms in *ortho*-position to the two phenyl rings and therefore it must not be influenced by the presence of the chlorine atom in *para*-position to one of the two rings.

For the same reason when 2-chlorostilbene was considered, it was assumed for phenyl B $\vartheta' = 0°$ in the *trans*- and $\vartheta' = 24°$ in the *cis*-isomer. For phenyl A in the first case, a twisting angle of 30° was obtained, due to the interaction between the chlorine atom in 2a-position and the hydrogen atom in α-position. It is clearly observable from the molecular models that one of the two *ortho*-positions is sterically more hindered than the other and the conformer with the chlorine in 2b-position would be more twisted and therefore energetically less probable. In the second case the greater twisting angle for phenyl A (38°) would indicate a probable presence of the conformer with the chlorine atom in 2b-position; a comparison of the sequences of theoretical and experimental dipole moments of the two isomers (Tab. 4) seems also to confirm this supposition.

In the case of the α,α'-dichlorostilbene the twisting angle was found greater in the *trans*-isomer (41°) than in the *cis*-isomer (34°); this result reproduces the phenomenon already observed for the α,α'-dimethylstilbene [*11*] and indicates that the α-substituents interact more strongly with the hydrogen in *ortho*-position to phenyl B than with the hydrogen in *ortho*-position to phenyl A. The angle of 34° for *cis*-α,α'-dichlorostilbene is consistent with the angle of 30° for *trans*-2-chlorostilbene; the slight disagreement is probably due to small differences in the distances between the two substituents (hydrogen and chlorine) in 2a- and α-position; such distances would coincide only if the $C_{\text{ethyl.}}$–H and C_{phenyl}–H distances were supposed to be equal with a rather arbitrary value of 120° for all bond angles at the carbon atoms.

The twisting angle in *cis*-α-chlorostilbene resulted higher respect to expectation (40° instead of 30—34°). The values obtained for the *trans*-isomer are of a still more difficult interpretation: the rotation of the phenyl rings was expected to be 30—34° for phenyl A and 40° for phenyl B; calculated values are lower, while the dipole moment results higher than the observed value.

Nevertheless, it may be concluded that the results of the calculation, although subject to the intrinsic limitations of the very simple method adopted and the approximations made, are in good agreement with the experimental data. It is our intention to extend the study to other halogenostilbene derivatives, provided other experimental data become available for suitable comparisons.

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