A STERIC CONFORMATIONAL ANALYSIS OF *CIS*- AND *TRANS*-STILBENE

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Possible conformations of *cis*- and *trans*-stilbene are analyzed using a combination of the Coulson nad Senent and the SC LCAO MO methods. The discussion involves the ground state, the first excited state and the ionic state.

In the case of the ground state only one stable *cis*-conformation is predicted, of a C_2 symmetry. On the other hand two stable *trans* conformations seem to exist which differ very slightly in energy. Their symmetry properties are C_2 and C_i accordingly. The predicted *trans* to *cis* barrier (35.4 kcal/mole) is in a good agreement with experiment: 36.7 kcal/mole for a liquid and 42.8 kcal/mole for a vapour. Also the estimated difference of the *cis* and *trans* isomers (3.3 kcal/mole) is in a good agreement with the experimental one (3–6 kcal/mole). The latest results of other authors [14]–[15] are not consistent with experiment: according to them the *cis* conformation should be more stable than the *trans* one.

1. Introduction

Several properties of *cis*- and *trans*-stilbene are closely related to its structure. However, so far theoretical approaches seem to be unsatisfactory in this respect. Let us begin with a short review of experimental and theoretical results which are related to the presented work.

X-ray data are known for the *trans*-stilbene only [1]. They are, however, rather old, and may require a revision. In theoretical calculations mostly a planar form is assumed, in agreement with the *X*-ray results. Discussing *cis*-stilbene one usually assumes a twisting around the "single" bonds by *ca* 30°, in analogy to the known *X*-ray structure of *cis*-azobenzene [2].

The melting points of *trans*- and *cis*-stilbene differ appreciably: 125°C and 1°C accordingly [3]. Therefore a large strain energy is likely in the case of the *cis*-stilbene crystal.

Some information is obtained from the analysis of the UV absorption spectrum. Out-of-plane deformations cause a blue shift, a hypochromic effect and a change of the

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shape of the bands [4]–[8]. The authors claim that *cis*- and *trans*-stilbene molecules are not planar, the non-planarity of *cis*-stilbene being larger.

It is interesting to note that the central "double" bond is more stable in *cis*-stilbene than in the *trans* case. Such a conclusion follows from the analysis of the vibrational structure of the first absorption band [6].

The oldest quantum-chemical estimate of the geometry of *cis*-stilbene is that given by Adrian [9]. With this purpose in mind he considered the π-electronic delocalization energy and the interaction energy between nonbonded atoms (*vdW* energy, for brevity).

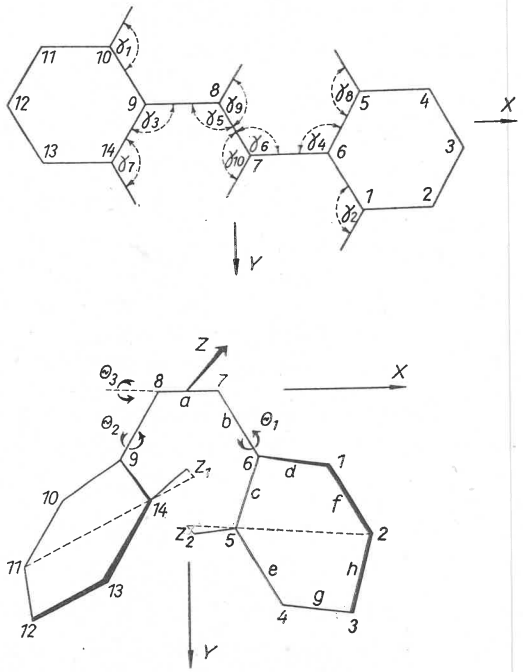

Fig. 1. Numbering of atoms and definition of independent coordinates

According to him $30° \leqslant \theta_1, \theta_2 \leqslant 40°$ (Fig. 1). The discussion given later by Rasch [10] was also based on the Hückel method. Assuming rather arbitrarily that $\theta_1 = \theta_2 = 2\theta_3$ (Fig. 1) he tried to fit these angles from a correlation of calculated and observed properties. According to Rasch $\theta_1 = \theta_2 = 26° \pm 4°$ and $\theta_3 = 13° \pm 2°$. A similar discussion of *cis*-stilbene was given by Beveridge and Jaffé [11], but on the basis of the Pariser, Parr and Pople method. Assuming $\theta_3 = 0$ they have found a best reproduction of the UV spectrum for $\theta_1 = \theta_2 = 30°$. A rather an untypical assumption was made by Lindner and Mårtensson [12]. According to them $\theta_1 = \theta_2 = 0$ by assumption and only θ_3 and γ_5 (equal to γ_6) were varied. However, the authors predicted uncorrectly that the first band in *trans*-stilbene should lie at higher frequencies than that in *cis*-stilbene. A similar uncorrect result was also obtained by Basu [13].

An extensive analysis of the isomerization process was carried out by Borrell and Greenwood [14] on the basis of the Pople method. Their reproduction of the UV absorption and fluorescence spectrum and of the *trans* to *cis* barrier was rather good. They have also tried to explain some effects related to photochemical isomerization, photosensitized isomerization and phosphorescence. However, only the θ_3 angle was optimized in their calculations, the other structural parameters being taken over from the cited *X*-ray work. All *vdW* interactions were neglected completely. Thus, it is evident that the calculated paths of isomerization are not optimal. In fact their prediction that the *trans* form should be less stable than the *cis* one is apparently in disagreement with experiment.

The conformation of *cis*- and *trans*-stilbene was also investigated by Ljunggren and Wettermark very recently [15]. They have applied the CNDO/2 method to this purpose. Their results, however, seem not to be satisfactory. According to them the *cis* form should be more stable than the *trans* one. The calculated *trans* to *cis* barrier exceeds three times the experimental one. They also predicted a twisting of the two phenyl rings by 90° both for *cis*- and *trans*-stilbene. Such a large twisting is rather unrealistic. Let us recall that also in the case of biphenyl the CNDO/2 method leads to a twisting by 90° [16]. In the last case it is well known, however, that the predicted twisting is more than twice too large.

As follows from this short review, no analysis of the possible conformations of stilbene is known which would consider all essential interactions and all important distortions. In order to fill in this gap we have carried out an analysis with what is called a self-consistent steric conformational method [17]. Several successfull applications of the method [18]–[20] made us believe that the results should be adequate.

2. Method

The self-consistent steric conformational method has been described elsewhere [17]. We summarize, therefore, only the main assumptions.

The dependence of the σ- and π-electronic energies on the bond lengths and large twisting angles was calculated with and extended Longuet-Higgins and Salem method [21]. All the remaining out-of-plane and in-plane distortions were treated with a modified Coulson and Haigh method [17], [22]. The problem was then to minimize the total energy of the system:

$$E_{\text{tot}} = \frac{2}{b} \sum_{i<j}^{\text{neighbours}} \left(\frac{1}{x} - a + R_{ij} \right) \beta_{ij}(R_{ij}, 0°) +$$

$$+ \tfrac{1}{2}\, \gamma \boldsymbol{K}_\gamma \gamma^T + \sum_{i=1}^{N} q_i \alpha_i + 2 \sum_{i<j}^{\text{neighb.}} p_{ij} \beta_{ij}(R_{ij}, \theta_{ij}) +$$

$$+ \tfrac{1}{2}\, z \boldsymbol{K}_z z^T + W + \text{constant}, \qquad (1)$$

where the first sum represents the dependence of the σ-electronic energy on the bond lengths, the next one its dependence on valence angles, the third and fourth sum represent

the π-electronic energy as dependent on large twisting angles, the next sum gives the distortion energy due to remaining out-of-plane deformations, W is the sum of all important *vdW* interactions (46 in stilbene). The meaning of the symbols is here standard: $\beta_{ij}(R_{ij}, \theta_{ij})$ is the resonance integral for the bond length R_{ij} and the twisting angle θ_{ij}, q_i is the number of π-electrons at atom i, p_{ij} is the mobile bond order, α_i is the Coulomb integral, $z = [z_1, z_2]$ is the row-vector of out-of-plane deformations defined for stilbene in Fig. 1, $\boldsymbol{K}_z$ is the matrix of appropriate force constants, $\gamma = [\gamma_1, \gamma_2, \ldots, \gamma_{10}]$ is the vector of in-plane deformations defined for stilbene in Fig. 1, $\boldsymbol{K}_\gamma$ is the appropriate matrix of force constants. Calculating W Bartell's formulae [23] were used for the H...H and C...H interactions and Dashevsky and Kitaygorodsky's one for the interactions between non-bonded carbon atoms [24]. The symbols a, b, x represent empirical parameters. In this method $a = 1.517$ Å, $b = 0.18$ Å and $x = 4.1/$Å [17].

The minimalization of E_{tot} is carried out under the condition that

$$\beta_{ij}(R_{ij}, \theta_{ij}) = \beta_0 \exp[-x(R_{ij}-1.397)] \cos\theta_{ij} \qquad (2)$$

where $\beta_0 = -1.403$ eV [17].

3. *Properties of the ground state*

The structural parameters which were found for the two stable *trans* conformations (C_i and C_2), the unstable *trans* conformation (C_{2h}), the stable *cis* conformation (C_2) and the unstable twisted case with $\theta_3 = 90°$ are listed in Table I. The *cis* conformation of the C_s symmetry shows no minimum of the total energy. As follows from the Table I the central bond length should be shorter in *cis*-stilbene than in *trans*-stilbene. This result

TABLE I

The structure of stilbene

Parameter	Ground state					Excited state		Ion	
	cis (C_2)	$\theta_3 = 90°$	*trans* (C_i)	*trans* (C_2)	*trans* (C_{2h})	*cis*	*trans*	*cis*	*trans*
$\theta_1 = \theta_2$	43°45′	0°03′	12°26′	13°46′	(0)	3°18′	0°00′	26°10′	0°00′
θ_3	4°25′	(90°)	180°00′	177°52′	(180°)	64°57′	180°00′	19°06′	180°00′
$\gamma_1 = \gamma_2$	120°02′	120°11′	120°12′	120°11′	120°11′	120°11′	120°16′	120°08′	120°16′
$\gamma_3 = \gamma_4$	121°14′	121°09′	122°35′	122°29′	122°52′	121°29′	122°46′	121°58′	122°50′
$\gamma_5 = \gamma_6$	124°50′	122°05′	123°58′	123°50′	124°21′	123°18′	124°25′	126°37′	124°24′
$\gamma_7 = \gamma_8$	120°15′	120°30′	120°58′	120°55′	121°05′	120°34′	121°08′	120°30′	121°07′
$\gamma_9 = \gamma_{10}$	117°38′	118°03′	119°15′	119°21′	119°08′	117°23′	118°46′	116°14′	118°58′
R_a	1.350	1.522	1.359	1.359	1.361	1.514	1.458	1.412	1.407
R_b	1.498	1.396	1.476	1.476	1.474	1.398	1.405	1.451	1.437
R_c	1.402	1.434	1.407	1.407	1.408	1.434	1.440	1.419	1.425
R_d	1.399	1.432	1.403	1.403	1.404	1.432	1.437	1.416	1.421
R_e	1.396	1.385	1.394	1.394	1.394	1.384	1.382	1.389	1.385
R_f	1.397	1.385	1.396	1.396	1.396	1.385	1.383	1.390	1.388
R_g	1.397	1.407	1.400	1.399	1.399	1.407	1.410	1.404	1.405
R_h	1.398	1.406	1.397	1.397	1.398	1.406	1.410	1.404	1.405
$z_1 = z_2$	0.03	0.00	0.025	0.028	0.00	0.017	0.00	0.059	0.00

is in agreement with the experimental result obtained by Dyck and McClure [6]. According to our calculations $\theta_3 = 4.5°$ in *cis*-stilbene. Thus Beveridge and Jaffé's assumption that $\theta_3 \approx 0°$ in *cis*-stilbene seems to be well justified. The twisting of the two almost single bonds is relatively small in *trans*-stilbene ($\theta_1 = \theta_2 = 12°–14°$) and quite large in *cis*-stilbene ($\sim 44°$). In the case of solutions the twisting angles will be smaller of course. Note finally that always $R_c > R_d$, the inequality being caused by the *vdW* interactions.

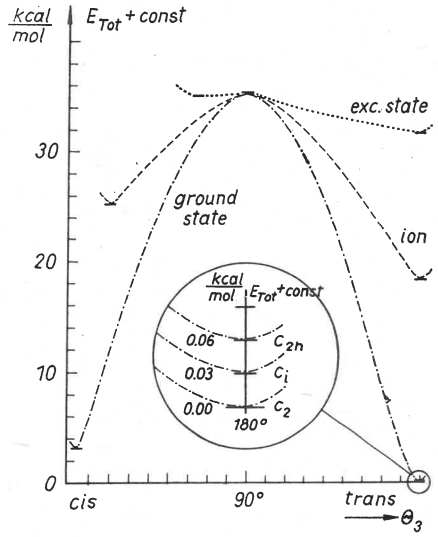

Fig 2. Dependence of the total energy on the twisting angle of the central bond for the ground state, the first excited state and the ionic state

According to the old *X*-ray data on *trans*-stilbene [1] $R_a = 1.33$ Å, $R_b = 1.45$ Å and $\gamma_5 = \gamma_6 = 128°$, all the other valence angles being assumed (120°). Certainly a variation of the other valence angles would result in a decrease of γ_5 and γ_6. Our numbers are as follows: $R_a = 1.36$ Å, $R_b = 1.475$ Å and $\gamma_5 = \gamma_6 = 124°$.

The dependence of the total energy on the twisting angle of the central bond is reproduced in Fig. 2. We recall that for any value of twist all the other structural parameters (Fig. 1) have been optimized. The equivalence of both phenyl rings followed from the calculations; it was not assumed. We see from Fig. 2 that the estimated barrier for the *trans* to *cis* isomerization is equal to 35.4 kcal/mole, in a fair agreement with the experimental results: 42.8 kcal/mole for the gaseous phase [25] and 36.7 kcal/mole for solutions [26]. *Trans*-stilbene is predicted to be more stable by 3.3 kcal/mole. This result compares favourably with the experimental estimates: 3 kcal/mole [25] or 6 kcal/mole [27].

The two stable *trans* conformations are equivalent in practice, as $E_{tot}(C_i) - E_{tot}(C_2) = -0.03$ kcal/mole. Also the barrier is negligible: $E_{tot}(C_{2h}) - E_{tot}(C_2) = 0.06$ kcal/mole. Therefore a strong vibronic coupling is expected.

The decomposition of the strain energy of *cis*-and *trans*-stilbene into various contributions is given in Table II.

TABLE II

Contribution to E_{tot} relative to the appropriate contribution for *trans*-C_2-stilbene (in kcal/mole)

Conformation	ΔE_{tot}	ΔE_σ	ΔE_π	ΔE_γ	ΔE_z	ΔW
twisted with $\theta_3 = 90°$	35.39	−13.16	51.45	−0.91	−0.03	−1.96
cis	3.27	3.92	1.88	−0.05	−0.00	−2.47
trans-C_{2h}	0.06	−0.80	−0.08	0.39	−0.03	0.58
trans-C_i	0.03	−0.13	−0.07	0.10	−0.00	0.13

4. Properties on the cation and the anion

The self-consistent steric conformational analysis, in its present form, does not invalidate the pairing theorem known for alternant hydrocarbons. Therefore all calculated properties refer equally well to the anion and to the cation, except the sign of net charges.

Internal coordinates of the stilbene ion conformations are given in Table I. There is one stable *trans* conformation only, which is planar. The *cis* form is not planar again, the twisting of the three internal bonds being comparable.

The path of isomerization in the ionic state is given in Fig. 2. The constant term in E_{tot} is here different from that for the ground state, differing by $\pm \alpha_0$. As follows from the figure the barrier of isomerization is now approximately half as large as in the ground state, the *trans* form being more stable again.

The distribution of the net charges, ϱ_i, depends on the conformation. Considering the cation, for example, we have obtained the following:

a) for the case of *cis* conformation

$$\varrho_1 = 0.061,\ \varrho_2 = 0.007,\ \varrho_3 = 0.095,\ \varrho_4 = 0.007,$$
$$\varrho_5 = 0.061,\ \varrho_6 = 0.056,\ \varrho_7 = 0.214,$$

b) for the case of *trans* conformation

$$\varrho_1 = 0.071,\ \varrho_2 = 0.007,\ \varrho_3 = 0.106,\ \varrho_4 = 0.006,$$
$$\varrho_5 = 0.070,\ \varrho_6 = 0.056,\ \varrho_7 = 0.182.$$

5. Properties of the first excited state

The isomerization of stilbene through the excited state is still unexplained. It would be very tentative, therefore, to discuss the energy map for the excited states. However, our self-consistent conformational analysis, in its present form, does not distinguish between the singlet and triplet excited states. Keeping in mind this severe limitation we have carried out such an analysis for the first excited state. The calculated structural data are given in Table I and the estimated isomerization path is reproduced in Fig. 2. As follows from the figure, the barrier of isomerization seems to be very small in this case. This

result is consistent with the model *A* of the photoisomerization of stilbene, as given by Stegemeyer [28].

A more detailed analysis of the isomerization process is required, however. It should be based on a full energy map and on a more advanced quantum-chemical treatment. Such an analysis will be carried out in a separate paper.

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