

ON THE ELECTRONIC ABSORPTION SPECTRUM OF *TRANS*-
AND *CIS*-STILBENE

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A reinterpretation of the electronic absorption spectrum of *trans*- and *cis*-stilbene is given. The SCF CI method in a modified Pariser, Parr and Pople version is applied to this purpose, with inclusion of steric effects. The hypsochromic effect due to the passage from solution to the gaseous phase is described quantitatively. The diagram of energy levels in *cis*- and *trans*-stilbene is consistent with the mechanism of fluorescence and phosphorescence, as suggested by Pariser.

1. Introduction

Owing to steric effects *cis*- and *trans*-stilbene molecule is expected not to be planar. The nonplanarity of the molecule influences the absorption spectrum [1]–[5]. It is certainly interesting to discuss this effect theoretically. This is just the purpose of the present paper.

Several papers have been devoted to the interpretation of the UV spectrum of *trans*- and *cis*-stilbene. The results are not always consistent. Let us analyze the most recent articles rather briefly. All of them are based on certain modifications of the Pariser, Parr and Pople method.

Beveridge and Jaffé [6] assumed a most regular and planar conformation of *trans*-stilbene. In the case of *cis*-stilbene they assumed that $\theta_3 = 0^\circ$, $\theta_1 = \theta_2 \neq 0^\circ$ (Fig. 1), the θ_1 angle serving as an empirical parameter. The π -electron repulsion integrals g_{ij} were evaluated from the uniformly charged spheres model. Their results are shown in Fig. 2a-b.

Perkampus and Knop [7] discussed also the spectrum of both isomers. They assumed a most regular planar conformation in each case and the Mataga-Nishimoto (MN) formula for the repulsion integrals, g_{ij} . Their results for *cis*-stilbene are shown in Fig. 2d.

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The results for *trans*-stilbene are similar to those shown in Fig. 2c which have been taken from a more recent work [8].

Wettermark, Tegner and Mårtensson [8] discussed the *trans* form only, assuming a planar conformation again. Their analysis was very detailed indeed and two different approximations of the g_{ij} integrals were investigated. The best results are reproduced in Fig. 2c. They refer to the case when the Mataga-Nishimoto formula was used. The authors give also references to the earlier works.

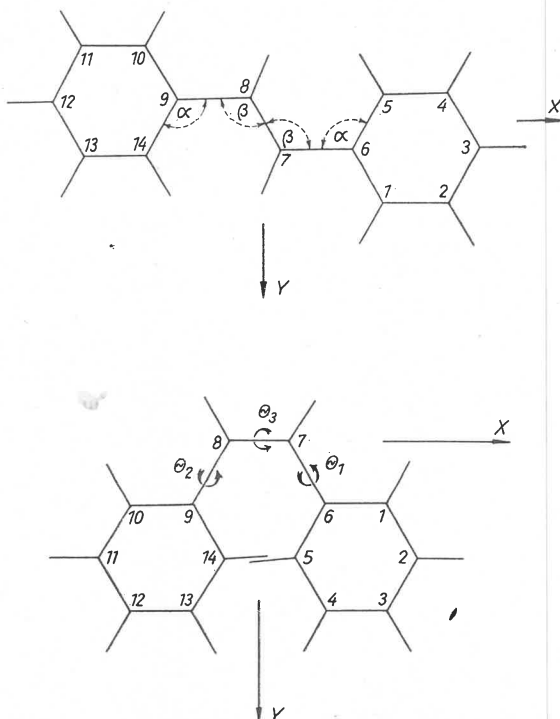


Fig. 1. Numbering of atoms and definition of internal coordinates

The planar case of *trans*-stilbene was also investigated by Adams and Miller [9]. In contrast to the other works their calculation was based on orthogonalized atomic orbitals. However, g_{ij} integrals in the orthogonalized basis have been approximated by the MN formula again. Their results seem not to be better than the preceding ones.

It might appear from Fig. 2 that the best agreement with experiment was obtained by Beveridge and Jaffé. However, the calculated ratio of oscillator strengths of bands A, B and C of *trans*-stilbene, 1 : 0.98 : 1.46, does not agree with the observed one, 1 : 0.36 : 0.59 [8]. The ratio obtained by all the authors who have used the MN approximation formula is in a better agreement with experiment (Wettermark *et al.* — 1 : 0.50 : 0.45; Perkampus and Knop — 1 : 0.34 : 0.33; Adams and Miller — 1 : 0.46 : 0.47; in our work — 1 : 0.50 : 0.44). The interpretation of the transitions as given by Beveridge

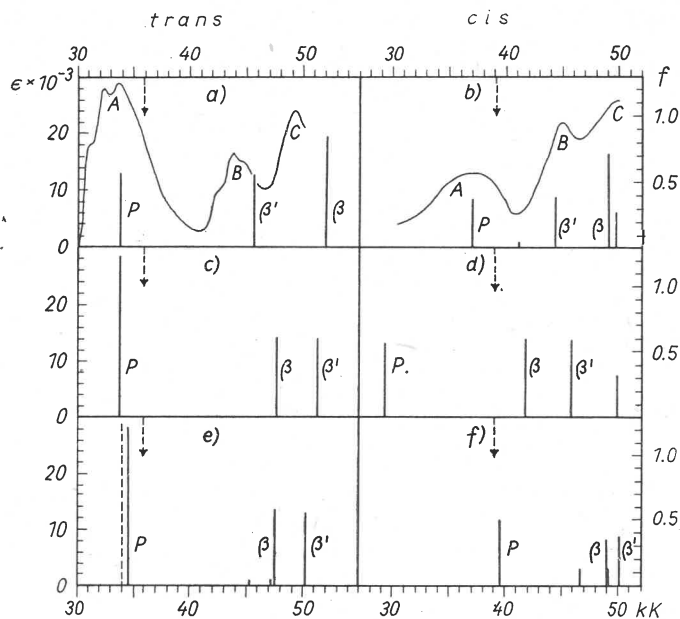


Fig. 2. Comparison of the calculated and observed spectrum of *trans*- and *cis*-stilbene. The dotted line gives the position of the first band in vapour. Figures a and b show the results obtained by Beveridge and Jaffé [6], figure c — by Wettermark *et al.* [8], figure d — by Perkampus and Knop [7]. Present results are shown in figures e and f.

and Jaffé and also by Adams and Miller differs from that given by other authors and in the present work. Let us recall therefore that Beveridge and Jaffé's assignment of the *B* band in the related *trans*-azobenzene is in disagreement with experiment [10].

2. Method

The calculations were carried out in the Pariser, Parr and Pople approximation within the SCF CI scheme. However, effects due to nonplanarity were included. The resonance integrals were calculated in accordance with formula (1),

$$\beta_{ij} = -2.318 \exp [-2.1888 (R_{ij} - 1.397)] \cos \theta_{ij} \text{ [eV]} \quad (1)$$

where R_{ij} is the bond length in Å, θ_{ij} is the twisting angle of the bond $i-j$. In the case of Coulomb repulsion integrals g_{ij} the MN formula was used. However, a correction due to nonplanarity was included [11]. In configuration interaction 36 lowest singly excited states were considered. In contrast to the previous calculations an optimal geometry of the two isomers was assumed, as following from the selfconsistent steric conformational analysis [12, 13]. The most significant structural parameters are listed in Table I. The symbols are explained in Fig. 1. For the remaining valence angles 120° was assumed. Bond lengths in the phenyl rings were taken close to 1.40 \AA [12].

Let us recall that the method yielded satisfactory results in the case of biphenyl [14] and butadiene [15].

TABLE I

Structural parameters for *cis*- and *trans*-stilbene

Parameter	<i>cis</i> (C_2)	<i>trans</i> (C_2)	<i>trans</i> (C_{2h})
θ_1, θ_2	43°45'	13°46'	0°
θ_3	4°25'	177°52'	180°
α	121°14'	122°29'	122°52'
β	124°50'	123°50'	124°21'
R_{78}	1.350	1.359	1.361
R_{67}, R_{89}	1.498	1.476	1.474

3. Results

In Fig. 2 the observed spectrum of *trans*- and *cis*-stilbene in solution is given. Passing over to the gaseous phase one observes a distinct hypsochromic shift of the *A* band both in the case of *trans*-stilbene [4, 5] and in the case of the *cis*-form [5]. The position of the appropriate maximum is denoted in Fig. 2 by a broken arrow.

The results of the present calculations are depicted in Fig. 2e-f. In table II we give the experimental and calculated transition energies, the calculated oscillator strengths, the predicted polarizations (defined in Fig. 1) and the principal contributions to the excited states in terms of the zeroth order CI wave functions.

As follows from Fig. 2e-f and Table II the calculated position of the maximum of the band *A* is in a good agreement with the observed one for both isomers in the gaseous phase. The position of the other two bands is not known experimentally.

TABLE II

Electronic absorption spectrum of *trans*- and *cis*-stilbene

<i>trans</i> - stilbene			<i>cis</i> - stilbene		
ΔE_{exp} (eV)	ΔE_{calc} (eV), f_{calc} and approximate polarization	approximate character	ΔE_{exp} (eV)	ΔE_{calc} (eV), f_{calc} polarization	approximate character
4.21 ^a	A) planar case B) C_2 -case 4.23(1.233, x) 4.31(1.195, x)	$V_{1,1}^+$ (97%)		4.62(0)	$V_{1,2}^-$ (60%)
4.46 ^b	4.44(0) 4.46(0)	$V_{1,2}^-$ (70%)	4.83 ^b	4.62(0)	$V_{1,3}^-$ (60%)
	4.44(0) 4.46(0)	$V_{1,3}^-$ (70%)		4.56 ^c	4.91(0.495, x)
	5.58(0) 5.62(0.000, z)	$V_{1,4}^+$ (81%)	5.58 ^c	5.78(0.114, y)	$V_{1,4}^+$ (76%)
	5.60(0) 5.63(0)	$V_{1,4}^+$ (92%)		5.80(0)	$V_{1,4}^-$ (90%)
	5.83(0) 5.87(0.046, z)	$V_{1,3}^+$ (97%)	6.20 ^c	6.08(0.354, xz)	$V_{1,3}^+$ (89%)
5.42 ^a	5.88(0.620, y) 5.91(0.583, y)	$V_{1,2}^+$ (95%)		6.11(0.112, y)	$V_{1,2}^+$ (96%)
6.13 ^a	6.24(0.554, x) 6.24(0.559, x)	$V_{2,3,2',3'}^+$ (78%)		6.21(0.379, x)	$V_{2,3,2',3'}^+$ (76%)
	6.43(0) 6.45(0)	$V_{1,5}^-$ (94%)		6.38(0)	$V_{3,4}^-$ (45%)

^afrom [2] (in solution), ^bfrom [5] (in vapour), ^cfrom [7] (in solution).

In solutions the molecule is certainly expected to be less distorted. Comparing Fig. 2d (for the planar case) and 2f (for the isolated distorted molecule) one can see, however, that transitions p , β and β' depend very strongly on nonplanarity. Therefore for $0^\circ < \theta_1$, $\theta_2 < 44^\circ$ the predicted position of the bands A , B , C should lie somewhere between that shown in Fig. 2d and 2f. Certainly there is such a value of twist for which also the experimental spectrum of the solution would be reproduced well with our method.

Let us also note that the calculated ratio of oscillator strengths of the band A for *cis*- and *trans*-stilbene, 1 : 2.414, is in a good agreement with the ratio observed, 1 : 2.260 [16]. The ratio obtained by Beveridge and Jaffé was definitely worse (1 : 1.569).

According to our calculations one should expect an inversion of the "plus" state and the "minus" state when passing from one isomer to the other. It follows from Table II that in the case of *trans*-stilbene the lowest excited singlet state is a "plus" state. In the case of *cis*-stilbene it is a "minus" state. The result is in accordance with the model of fluorescence of stilbene as suggested by Pariser [17].

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