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The π-Electron Energies of *Cis*- and *Trans*-Stilbene*

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π-electron energies of *cis*- and *trans*-stilbene and the benzyl radical have been calculated by use of the semiempirical method proposed by PARISER, PARR and POPLE. Special attention is devoted to differences in total energies between the two isomers and to the steric hindrance in the *cis*-form.

Mit der PPP-Methode wurden die π-Elektronenergien von *cis*- und *trans*-Stilben und dem Benzylradikal berechnet. Spezielle Aufmerksamkeit wurde auf den Unterschied der beiden Isomere bezüglich der Gesamtenergie und der sterischen Hinderung gerichtet.

Les énergies des électrons π du *cis* et du *trans*-stilbène ainsi que du radical benzyle ont été calculées à l'aide de la méthode semi-empirique de Pariser, Parr et Pople. On étudie particulièrement les différences des énergies totales entre les deux isomères et l'empêchement stérique de la forme cis.

Introduction

The *cis* and *trans*-isomers of the stilbene molecule have been treated by many authors (see e.g. [*1*—*8*]). There exists, however, no theoretical treatment which satisfactorily explains at the same time the energyspectra, the steric form of the *cis*-isomer and the *cis*-*trans*-conversion mechanism.

One of the reasons for this is that the geometry of *cis*-stilbene is not experimentally exactly known. It is obvious from steric reasons that it cannot be obtained from the *trans*-form by a simple rotation of 180° around the ethylene bond between the two phenyl groups. Indeed planarity of *cis*-stilbene requires an increase of the ethylenic angles from 128° to about 155°.

The steric strain in *cis*-stilbene could be released either by a rotation of 40° around the double bond $\alpha\alpha'$ or a rotation of 25° around each of the single bonds α 1 and $\alpha'1'$ (Fig. 1). Many authors prefer a rotation around the single bonds, this is supported mainly by spectroscopic arguments (see e.g. [*5*—*8*]). However there has to be a rotation around the $\alpha\alpha'$ bond in the transition state in order to get the *cis*-form from the *trans*-isomer. The changes in bond lengths due to these rotations are not included in the present calculation because of the extra complications involved.

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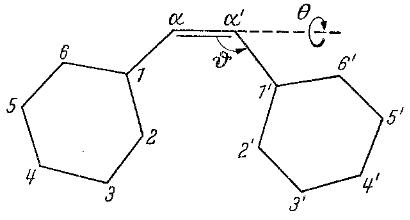

Fig. 1

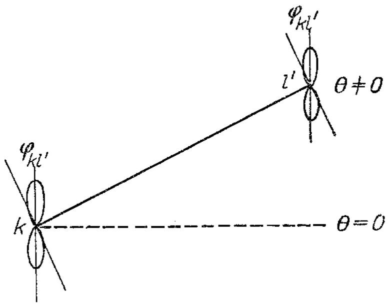

Fig. 2

Fig. 1. Numbering of the carbon atoms in *cis*-stilbene

Fig. 2. The angle $\varphi_{kl'}$. (The angele θ is the angle between the planes containing k(1, 2 ... 6) and l'(1', 2' ... 6') respectively. The planes intersect along the bond $\alpha\alpha'$)

Our intention has been to make a preliminary investigation of the dependence of the π-electron properties on the ethylenic angle and on the rotation around the bond $\alpha\alpha'$. In order to get an estimate of a possible transition state we also made a calculation on the benzylradical.

Table 1. *Calculated π-electron energies for stilbene (in* eV*)*

		Total ground state energy	First singlet transition	First triplet transition	Heat of reaction
Trans-stilbene		–557.999	5.814	5.132	0
Cis	(128; 20)[b]	–565.322	5.402	4.554	– 7.323
	(128; 25)[b]	–554.465	5.321	4.250	+ 3.534
	(128; 30)[b]	–542.005	5.274	3.804	+15.994
Cis	(128; 20; φ)[a]	–558.112	5.439	4.587	– 0.113
	(128; 25; φ)[a]	–544.901	5.365	4.289	+13.098
	(128; 30; φ)[a]	–530.706	5.317	3.841	+27.293
Cis	(128; 0)	–586.390	5.601	4.938	–28.391
	(140; 0)	–569.015	5.726	5.054	–11.016
	(150; 0)	–559.860	5.794	5.118	– 1.861
	(160; 0)	–554.491	5.848	5.122	+ 3.508
Exp.	*Trans*	—	3.89[c]	2.15[c]	+0.10 – + 0.15 [*19, 20*]
	Cis	—	4.43[c]	2.48 [*1*]	
benzylradical		–234.725	1.061	0.155	—
benzyl (+) ion		–203.298	3.244	2.367	—
benzyl (–) ion		–214.489	3.244	2.367	—

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[a] Corrected for nonplanarity ($\varphi_{kl'} \neq 0$).

[b] (128; 20) means $\vartheta = 128°$, $\theta = 20°$.

[c] Ref. [*3, 4, 5, 7, 16, 17, 18*].

Table 2. *Energies of the eight lowest molecular orbitals (in* eV*)*

	1	2	3	4	5	6	7	8
Trans-stilbene	−15.008	−14.697	−13.234	−11.439	−11.300	−11.298	−10.592	−0.598
Cis (128; 20)[a]	−14.936	−14.694	−12.878	−11.441	−11.306	−11.294	−10.377	−0.813
Cis (128; 25)[a]	−14.908	−14.696	−12.711	−11.445	−11.305	−11.295	−10.230	−0.960
Cis (128; 30)[a]	−14.881	−14.696	−12.538	−11.452	−11.303	−11.294	−10.031	−1.159
Cis (128; 0)	−15.014	−14.693	−13.235	−11.434	−11.308	−11.292	−10.600	−0.590
Cis (140; 0)	−15.016	−14.695	−13.234	−11.435	−11.303	−11.296	−10.590	−0.600
Cis (150; 0)	−15.018	−14.696	−13.234	−11.435	−11.302	−11.297	−10.585	−0.605
Cis (160; 0)	−15.009	−14.686	−13.233	−11.427	−11.301	−11.297	−10.571	−0.619

[a] Correction for non-planarity ($\varphi_{kl'} \neq 0^0$) gives only changes in the last figure.

Method of Calculation

The electronic structures have been calculated in the MO–LCAO-scheme, applying the semiempirical self-consistent method proposed by Pariser, Parr and Pople [*9, 10*]. This method is characterized by

a) the σ-π separation,
b) the zero-differential overlap approximation,
c) neglection of penetration integrals,
d) use of the Goeppert-Mayer-Sklar approximation [*11*].

The two center Coulomb integrals occurring have been approximated by the expression introduced by Ohno [*12*].

$$\gamma_{kl} = (kk \mid ll) = (R_{kl}^2 + \lambda_{kl}^2)^{-1/2} \tag{1}$$

where R_{kl} is the internuclear distance between atoms k and l and

$$\lambda_{kl}^{-1} = \tfrac{1}{2}\left[(I_k - E_k) + (I_l - E_l)\right]. \tag{2}$$

I_k and I_l are the ionization potentials and E_k and E_l are the electron affinities of atoms k and l respectively in their appropriate valence states. No configuration interaction treatment was done.

In *cis*-stilbene we assume one of the phenylrings to be rotated an angle θ around the $\alpha\alpha'$ bond. The dependence of $\beta_{kl'}$ and $\gamma_{kl'}$ on θ was introduced in the

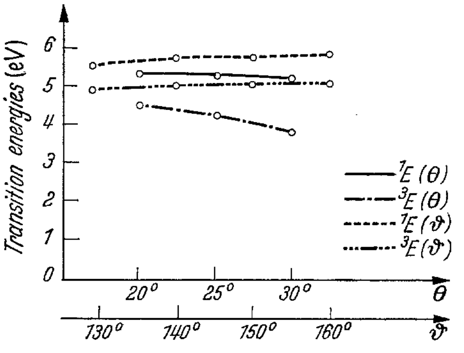

Fig. 3. Lowest singlet and triplet transition energies as functions of θ and ϑ

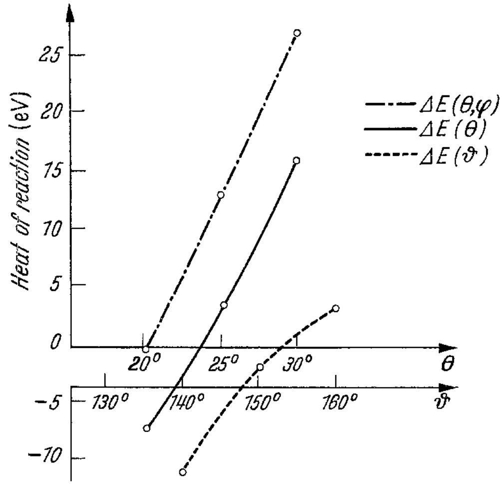

Fig. 4. Heat of reaction as function of θ and ϑ

usual way by multiplication with a $\cos\theta$- respectively a $\cos^2\theta$-factor [*22*]. Further in one of our calculations we made an approximate correction, for the non-planarity, through multiplying $\gamma_{kl'}$ by a $\cos^4 \varphi_{kl'}$-factor (Fig. 2).

The following experimental values were used in the calculations:

$E_c = 0.03$ eV [*13*], $I_c = 11.16$ eV [*13*]

$\beta_{\alpha\alpha'} = 3.35$ eV [*14*], $\beta_{1\alpha} = 1.69$ eV [*14*], $\beta_{12} = 2.39$ eV [*14*], for non-nearest neighbours $\beta_{\mu\nu} = 0$

$R_{\alpha\alpha'} = 1.33$ Å [*15*], $R_{1\alpha} = 1.45$ Å [*15*], $R_{12} = 1.39$ Å [*15*].

Bond angles: in phenyl rings 120° [*15*]; *trans*-stilbene is treated as planar with angle $\vartheta = 128°$ [*15*]. The investigated θ- and ϑ-values for *cis*-stilbene were $\theta = 20°$, 25° and 30° (for $\vartheta = 128°$) respectively $\vartheta = 128°$, 140°, 150° and 160°.

The results are reported in Tab. 1 and 2 and Fig. 3, 4 and 5.

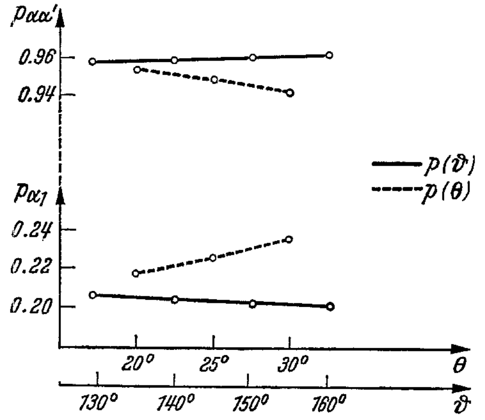

Fig. 5. Bond orders for $\alpha\alpha'$ and $\alpha 1$ as functions of θ and ϑ

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