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All-Electron SCF LCAO MO Calculations on Various Conformations of *cis*- and *trans*-Stilbene

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Ab initio SCF calculations of *cis*- and *trans*-stilbene at different conformations were performed using two program systems. Minimal energy is obtained for *cis*-stilbene when the phenyl rings are rotated by 52° out of the molecular plane. The deviation from planarity due to steric hindrance is smaller for the *trans* isomer yielding a rotational angle of 19°. The *trans* isomer is calculated to be more stable by 5.7 kcal/mole than the *cis* isomer, confirming the experimental estimate according to which the energy of isomerization is about 3 kcal/mole. This is an improvement over semiempirical calculations which predict a lower energy for the *trans* configuration.

Key words: Stilbene, conformations of *cis*- and *trans*-~

1. Introduction

The molecular structure of the ground and lowest excited states of *cis*- and *trans*-stilbene has been the subject of numerous studies in the last few years. Experimentally, the early X-ray structure determination [1] of *trans*-stilbene has been recently refined by several authors [2, 3]. In the gas phase the molecular structures of *cis*- and *trans*-stilbene were obtained by electron diffraction [4, 5]. In the solid state *trans*-stilbene is almost planar, with a rotational angle θ (cf. Fig. 1) of about 5°, which differs distinctly from that of the free molecule as measured in the gas phase, which is about 30°. Free *cis*-stilbene has a propeller-like conformation with C_2 symmetry [5], the deviation from planarity being larger than most calculations are able to predict. The various types of calculations performed until now have employed only semiempirical MO methods [7–21]. On the *ab initio* level, the calculation of styrene can be considered as a model case for *trans*-stilbene [22]. All of these investigations, although they yield a great deal of information on the ground

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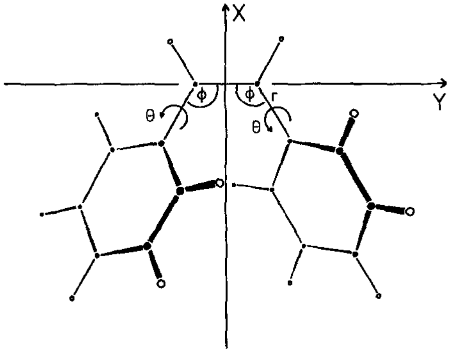

Fig. 1. Geometry of *cis*-stilbene, with the internal coordinates varied in the present work noted

and excited state structures, as well as spectral and photochemical properties, have not explained the higher stability of the *trans* over the *cis* isomer, having led to isomerization energies at odds with experience. Therefore, we thought it would be interesting to investigate by *ab initio* methods the stability, and also the conformational problem, performing extensive calculations with one of the largest sets of primitive basis functions which can be managed by a large computer.

2. Details of Calculation

2.1. Molecular Geometry

The phenyl rings are considered as regular hexagons. The C–C distances are set equal to 1.39 Å and the C–H distances equal to 1.08 Å; both were taken from various X-ray diffraction measurements [1–3]. From these results the central double bond length was chosen to be 1.32 Å and both C–Ph distances were taken equal to 1.46 Å. The valence angle ϕ and the rotational angle θ, which are varied in the present calculation, are defined as indicated in Fig. 1. For *trans*-stilbene a limited variation of the C–Ph distance r has also been investigated.

2.2. Basis Sets

In order to obtain an appropriate basis set with optimal flexibility and economy in computer time, some test calculations were performed on planar *trans*-stilbene using some of the basis sets given in the literature [23–28]. The basis sets were contracted in all cases to a [2.1/1] minimal basis set, resulting in 82 contracted Gaussian basis functions. Table 1 compiles the results obtained for four different basis sets. A comparison of total energies shows that the most efficient basis set, in relation to the number of primitive Gaussian-type functions, is that denoted by A, which uses the atomic basis set of Whitman and Hornback [23] for carbon, and the contracted basis function of Huzinaga [24] for hydrogen. The lower energies calculated by sets B and D result from better energies obtained for their atomic constituents, the molecular binding energies being nearly equal to those for A. Therefore it was decided to choose the basis set A for all calculations presented in the following.

Table 1. Test calculations, using several minimal basis sets, on planar *trans*-stilbene ($\theta = 0°$, $\phi = 120°$)

Basis set	Prim. GTFs per atom	Total no. of prim. GTFs	No. of unique integrals	E(a.u.)	$-V/T$
A Whitman and Hornback: C [23], Huzinaga: H [24]	(5.2/2)	178	745,386	−533.50125	2.011
B Clementi [25]	(7.3/3)	260	960,841	−534.84524	2.006
C Stewart, 3-term-expansion [26]	(6.3/3)	246	1,108,551	−529.33147	2.021
D Roos and Siegbahn: C [27], Clementi: H [28]	(7.3/3)	260	968,209	−535.17212	1.999

2.3. *Integral- and SCF-Calculations*

A list of unique integrals was generated using the symmetry transformation matrices of Dacre and Elder [29, 30] of the group C_2 for the *cis* isomer and C_{2h} for the *trans* isomer. A blocking of the Hartree–Fock matrix was obtained by constructing symmetry orbitals from linear combinations of the contracted Gaussian functions according to the transformation properties of the basis orbitals under C_2 and C_{2h} symmetry operations. The convergence criterion for the total energy was set at 10^{-8} a.u. Convergence problems due to oscillations of the total SCF energy in the calculations on *trans*-stilbene were removed, for all basis sets used, by averaging corresponding elements $R_{\nu\mu}$ of the first order density matrix over two successive iterations, p and $p+1$, according to

$$R_{\nu\mu}^{(p+2)}=\lambda\cdot R_{\nu\mu}^{(p+1)}+(1-\lambda)R_{\nu\mu}^{(p)}$$

No such oscillations occurred for λ coefficients smaller than 0.3, however the convergence rate was still very low. More than 400 iterations were needed in order to arrive at the limit. The unusually large number of iterations indicated that the convergence point (e.g. -532.7757 a.u. for the basis set A) was a shallow side-minimum, differing appreciably from the actual SCF limit for the ground state of *trans*-stilbene. Therefore, the application of other extrapolation methods was tried. However, neither the extrapolation technique proposed by Yoshimine and Veillard [31] for density matrices, nor the e_k-transformation procedure which extrapolates eigenvectors, [32] could lead to the absolute SCF limit; both methods again converged to the small side-minimum. The problem was solved by classifying the symmetry orbitals according to a lower group, i.e., to the subgroup C_2 of the point group of *trans*-stilbene. When using starting vectors constructed from SCF-MO coefficients as obtained for *cis*-stilbene at $\theta=75°$ (at this configuration the energies of *cis*- and *trans*-stilbene are very similar) which were appropriately corrected in sign according to the symmetry C_2, the SCF procedure converged to a lower minimum after fewer than 80 iterations (cf. Table 1).

The calculations were performed using two systems of programs, PHANTOM (QCPE-No. 241) and MANYATOM [33], the latter being a closed-shell CDC 7600 version of POLYATOM II. The average CPU time necessary on the Cyber 76 was 3500 sec for all calculations with the basis set A and about 6400 sec for all other basis sets. The maximum storage requirements were 8.5 K words of small core memory (SCM) and 38 K words of large core memory (LCM), both 60 bits word-length.

3. Results and Discussion

For predicting molecular configurations from energy calculations, the absolute minimum of a function $e(x_1, x_2, \ldots)$ must be determined, where the x_i are internal coordinates of the molecule. The degree of freedom for a molecule like stilbene is by far too large for this minimum to be calculated by an independent and simultaneous variation of all x_i parameters. In particular, for *ab initio* calculations only a limited number of configurations can be chosen, which must cover

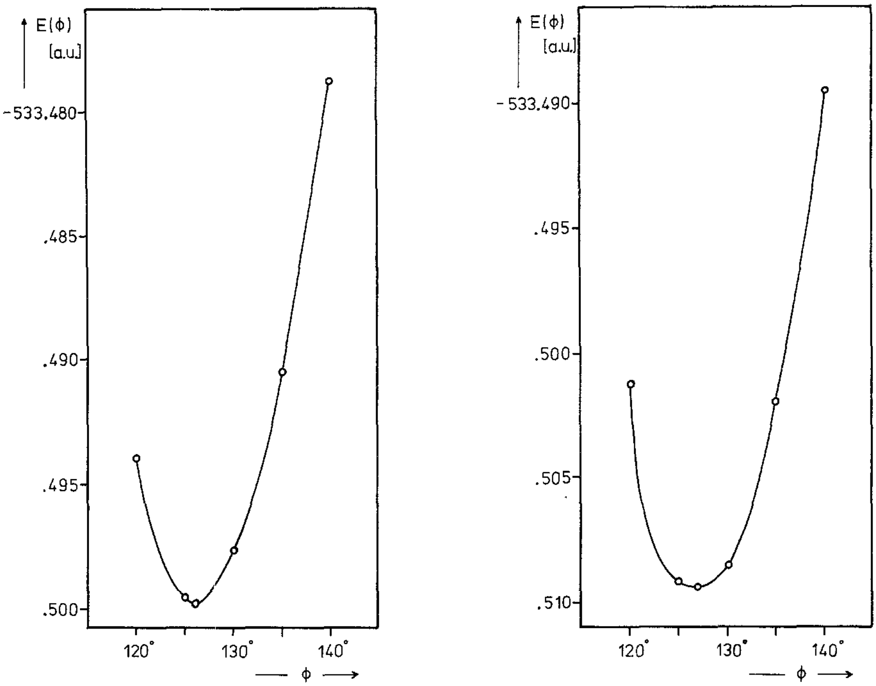

Fig. 2. Energy dependence $E(\phi)$ for (a) *cis*-stilbene at $\theta = 60°$ and (b) *trans*-stilbene at $\theta = 0°$

all important structural features of the molecule. In the ground state it is necessary to vary all parameters which are connected with bonds causing a certain geometric lability ("non-rigidity") of the molecule. The coordinates of rigid bonds (e.g. in the phenyl ring) are considered to be constant and may not be optimized. For stilbene the molecular parameters which ought to be optimized are those describing the conformation at the central double bond and the phenyl rings, i.e., the valence angle ϕ, the rotational angle θ, and eventually the C–C bond distance r, as denoted in Fig. 1. However, due to the large expense of computer time involved with *ab initio* calculation, a function of only two or three parameters cannot be correctly investigated in the described manner. Therefore a procedure must be followed defining a sequence of stepwise variations which leads to the absolute minimum as closely as possible.

As a guideline for such a procedure, usual valence angles, steric factors and different degrees of energy variations with respect to internal coordinates may be used. Since the valence angle for a carbon atom in a trigonal valence state is $\phi = 120°$, the calculation was started for *cis*-stilbene by varying the dihedral angle θ in the region 0°–90°, in steps of 15°, while keeping ϕ constant at this value. By applying quadratic interpolation a minimum was obtained at $\theta = 60°$ (cf. Fig. 3a). Next the valence angle ϕ was varied within 120°–140°, in steps of 5°, at a constant rotational angle of $\theta = 60°$. Minimal energy for the projection $E(\phi, \theta = 60°)$ onto the potential hypersurface was reached at $\phi = 126.2°$ (cf. Fig. 2a). At this ϕ angle the rotational angle was again optimized resulting in a value of $\theta = 52°$ for minimal energy (also

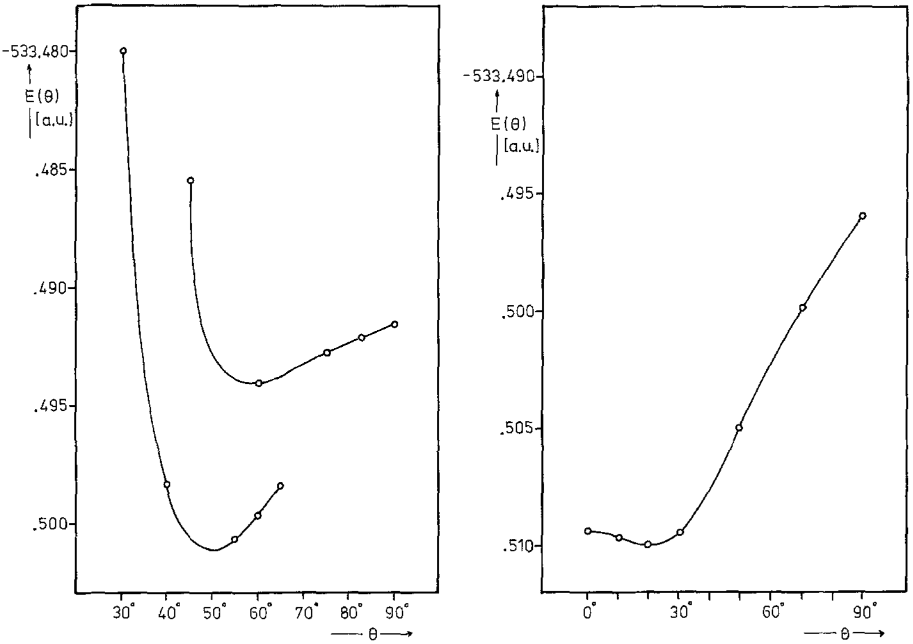

Fig. 3. Energy dependence $E(\theta)$ for (a) *cis*-stilbene at $\phi_1 = 120°$ and $\phi_2 = 126°$ and (b) *trans*-stilbene at $\phi = 127°$

plotted in Fig. 3a). Since the error becomes rather small, a further reoptimization was not carried out in view of the considerable expense necessary for each calculation.

As can be seen from the figures, the energy varies more rapidly with respect to ϕ than with θ. In the region close to the minimum the potential curve does depend only very little on θ. Two explanations, with opposite effects, can be presented in this connection: the steric hindrance of neighbouring hydrogen atoms in *cis*-stilbene with rotated phenyl rings is influenced much more by a change in ϕ than by rotating the phenyl rings further, since by this mechanism only projections onto the molecular plane (being identical with the plane of ϕ) are effective. On the other hand the π-electron system, which is little influenced by a change of ϕ, is decoupled by an out-of-plane rotation θ, increasing the total energy of the molecule. Accepting the classical model, which allows for a separation of σ- and π-electrons, it can be summarized that the size of the rotational angle θ results from a compromise between the steric hindrance due to the hydrogen atoms and the coupling of the π-electron system. The valence angle ϕ is primarily determined by the σ-electron system, which depends on the hybridization and also on the steric hindrance. The larger variation of energy with ϕ is manifested in correspondingly larger vibrational quanta for scissoring modes compared to torsional modes.

For *trans*-stilbene the effect of steric hindrance is, of course, smaller. The slight deviation from planarity must be explained by the repulsive force between ortho-hydrogen atoms of the phenyl rings and corresponding hydrogen atoms adjacent

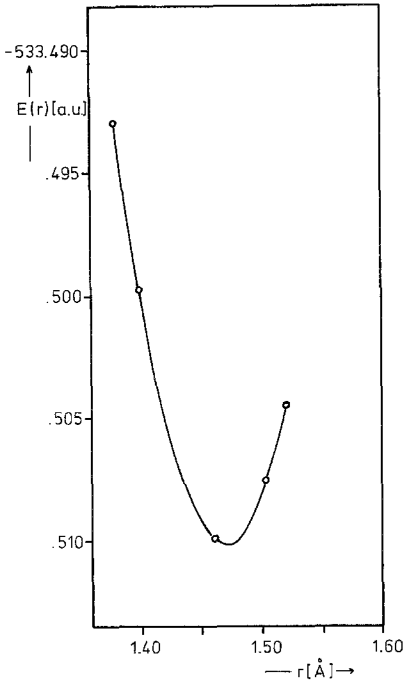

Fig. 4. Energy dependence $E(r)$ for *trans*-stilbene at $\phi = 127°$ and $\theta = 20°$

to the central double bond. Therefore the calculation on *trans*-stilbene was begun by varying ϕ at constant $\theta = 0°$. The functional dependence is presented in Fig. 2b. Minimal energy was obtained at $\phi = 127.4°$. Using $\phi = 127°$ the rotational angle θ was varied as given in Fig. 3b. By quadratic interpolation an optimal value of $\theta = 19°$ is calculated. Again, the energy change depends considerably more on the valence angle than on the rotational angle. From the steric arguments mentioned, the rotational angle in the *trans* isomer is smaller than for *cis*, and the projection $E(\theta, \phi = 127°)$ is almost entirely determined by the decoupling of the π-electron system.

For *trans*-stilbene also the energy dependence on the C–C distance r in ethylene and in the phenyl ring has been investigated. The calculated equilibrium position at $r = 1.47$ Å, as presented in Fig. 4, is very close to the experimental value, i.e. 1.46 Å, which was used in all other calculations in this paper.

Table 2 compares the present *ab initio* results with experimental data obtained for free molecules and with two recent semiempirical calculations. The agreement of all data for the valence angle ϕ is very good, and is probably caused mainly by the hybridization effect being well represented in all of the calculations. Less satisfactory is the calculation of the torsional angle θ, which for all semiempirical methods is too low. The *ab initio* calculations on *cis*-stilbene yield an angle significantly larger. However, since the potential curves are relatively flat with respect to this coordinate the equilibrium angle can vary about ± 10° at room temperature when one quantum, kT, is added to the system. This presumably is an explanation

Table 2. Comparison of experimental, semiempirical and *ab initio* data on stilbene

		cis-Isomer			*trans*-Isomer	
	Exp.[a]	semiemp.	*ab initio*	Exp.[a]	semiemp.	*ab initio*
$\theta°$	43.2 ± 3.2	~30[b] 38[c]	52	32.5 ± 3.1	20[c]	19
$\phi°$	130 ± 1	128[b] 128[c]	126	128 ± 1	128[b] 128[c]	127
C-Ph (Å)				1.46	1.45[b]	1.47
E_{tot} (a.u.)		−108.4815[b] −108.11265[c]	−533.50096		−108.479[b] −108.11068[c]	−533.50999

[a] Electron diffraction [4, 5].
[b] CNDO/2 calc. [8].
[c] NDDO calc. [21].

for the differing results in theory and experiment. Surprisingly good agreement between experimental and *ab initio* results are obtained for the energy of isomerization, which means a significant improvement over semiempirical calculations. From experimental data Kistiakowsky and Smith [34] estimated an energy of conversion of 3 kcal/mole, the *trans* isomer being more stable than the *cis* isomer. Neglecting the change in zero-point energy, the *ab initio* calculation yields an isomerization energy of 5.7 kcal/mole which is the difference of the (very large) molecular energies at their calculated equilibrium configurations (see Table 2). Semiempirical methods have calculated a higher stability for the *cis* isomer yielding −1.6 kcal/mole for the *trans–cis* isomerization in a CNDO/2 approximation [8], and −1 kcal/mole in a NDDO approximation [21].

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