A CNDO/2 Calculation on Stilbene*

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The equilibrium conformations of *trans*- and *cis*-stilbene and the rotational barrier between the two isomers were calculated using the CNDO/2 method. The results for the equilibrium angles and distances are in good agreement with experimental data. However, according to the calculations the phenyl rings would have a nearly free rotation which is only limited by steric hindrance. This result obviously deviates from the current view. The results are discussed in relation to previous theoretical and experimental evidence.

Die Gleichgewichtskonformation von *trans*- und *cis*-Stilben und die Rotationsbarriere zwischen zwei Isomeren wurde nach der CNDO/2-Methode berechnet. Die Ergebnisse in bezug auf die Geometrie stimmen mit experimentellen Daten gut überein, die Rotationsbarriere für die Drehung der Phenylringe dagegen ist praktisch Null.

La méthode CNDO/2 a été employée pour calculer les conformations d'équilibre du trans- et du cis-stilbène ainsi que la barrière de rotation entre ces deux isomères. Angles d'équilibre et distances calculés sont en bon accord avec les données expérimentales. Cependant les calculs indiquent que les cycles phényles devraient posséder une rotation libre soumise seulement à l'empêchement stérique. Ce résultat s'écarte de l'opinion courante. Les résultats sont discutés en relation avec les données théoriques et expérimentales antérieures.

Introduction

Stilbene often serves as a model substance in discussions of conformation (i.e. steric hindrance, π-conjugation, resonance energy) and *cis-trans* isomerization (e.g. rotational barrier, transition state, gas phase and liquid state kinetics). Consequently, this substance has been made the subject of numerous theoretical and experimental investigations. The quantum mechanical approximations previously applied to stilbene were originally developed for studies on planar systems, and serious objections can always be raised when they are adapted for the treatment on non-planar cases. As such conformations are likely to play a key-role in the chemistry of stilbene, it was considered most interesting to apply the lately developed CNDO method to the stilbene problem. The CNDO method is innately capable of treating non-planar conformations, offering an SCF treatment of all the valence electrons.

Santry's modification [5] of the CNDO/2 method was applied [1–5].

The phenyl rings of stilbene were assumed to be regular hexagons with C–C distances equal to 1.39 Å and C–H distances equal to 1.084 Å.
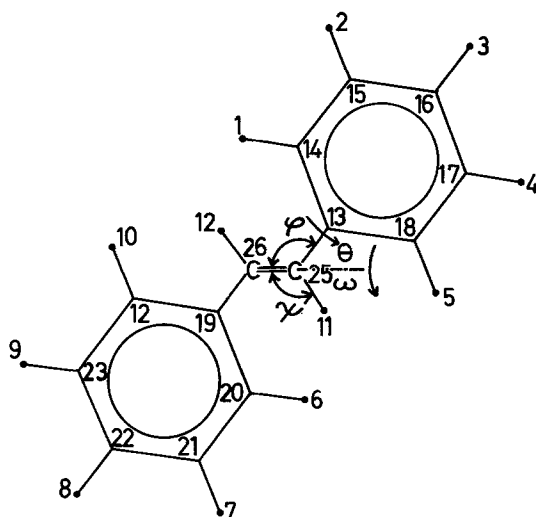

Fig. 1. Designation of the atoms and angles in the stilbene molecule

The central C–C double bond of the molecule was assumed to be 1.33 Å and the C–Ø distance (C_{19}–C_{26} and C_{13}–C_{25}) was taken as 1.44 Å except where otherwise specified. These values are the same as those found by Robertson and Woodward using X-ray diffraction [6].

The angles that were varied and the numbering of the atoms of the molecule appear from Fig. 1.

Results

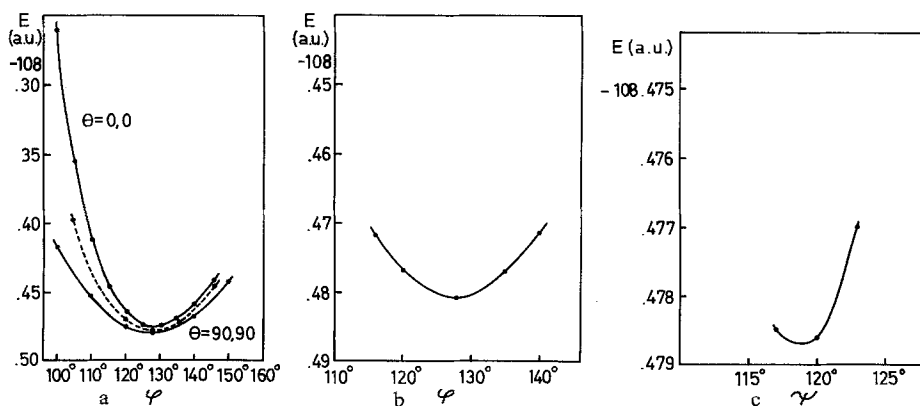The results of the calculations on stilbene are shown in Figs. 2–5.

Fig. 2. Energy of a *trans-* and b *cis*-stilbene as a function of the angle ϕ. c Energy of *trans*-stilbene as a function of the angle ψ

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[1] $\theta = a, b$ means that θ is equal to a for the left half of the molecule and equal to b for the right half of the molecule, cf. Fig. 1.

a) Equilibrium Conformations

The variation of the energy of *trans*-stilbene with the angle ϕ is shown in Fig. 2a. The three curves refer to $\theta = 0, 0$, $\theta = 90, 0$ and $\theta = 90, 90$ respectively[1]. For all points in Fig. 2a, the C–C double and the C–Ø single bond distances were set equal to 1.33 and 1.44 Å, respectively. Minimum energy is obtained for $\phi = 128°$, in excellent agreement with experimental results for the solid state obtained by X-ray diffraction techniques [6]. The fact that CNDO predicts a lower energy for the perpendicular ($\theta = 90, 90$) rather than for the planar conformation ($\theta = 0, 0$) was very surprising and is discussed at some length below. Furthermore, Fig. 2a shows that the energy difference between the planar and perpendicular conformations depends on the angle ϕ. This is readily explained as a result of steric interaction between hydrogen atoms (H_5–H_{11} and H_1–H_{12}) in the planar conformation. However, the fact that this steric interaction evidently has its minimum at the equilibrium angle $\phi = 128°$ does not explain why the same equilibrium angle is obtained for the perpendicular molecule. Very nearly the same angle is also obtained with *cis*-stilbene, Fig. 2b. In this figure, $\theta = 90, 90$, and the bond lengths are the same as above. We thus deduce that the value of ϕ is probably determined by the state of hybridization of the central carbon atoms rather than by steric factors.

Fig. 3a shows the variation of energy of *trans*-stilbene when one of the phenyl rings is rotated (angle θ) while the other ring is held fixed in the planar ($\theta = 0$),
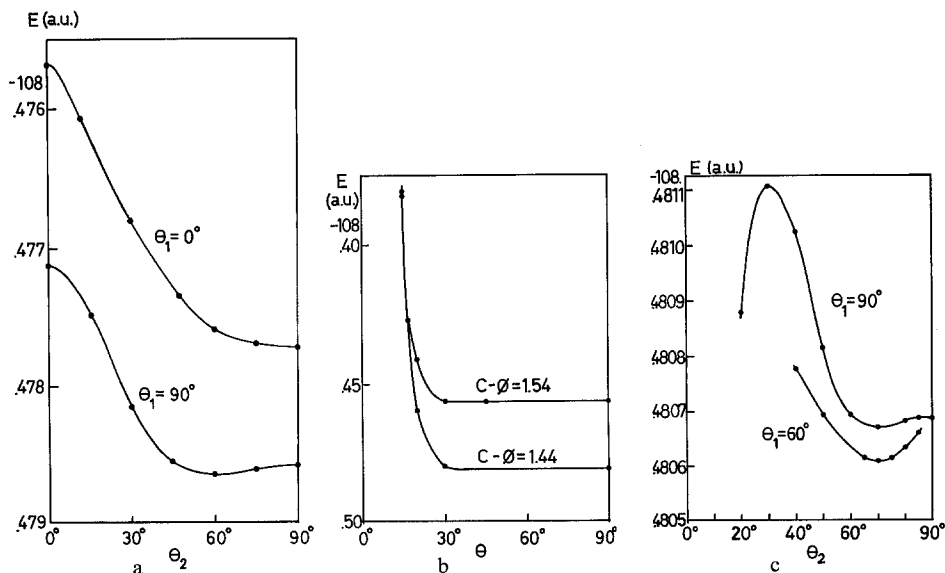

Fig. 3. a Energy of *trans*-stilbene as a function of θ for the right phenyl ring, the left ring being kept at $\theta = 0°$ (upper curve) or $\theta = 90°$ (lower curve). b Energy of *cis*-stilbene when both phenyl rings are rotated by an angle θ so that the molecule acquires a propellor-like shape. c Energy of *cis*-stilbene when the one phenyl ring is rotated by an angle θ, the other being held at $\theta = 60°$ (lower curve) and $\theta = 90°$ (upper curve) respectively
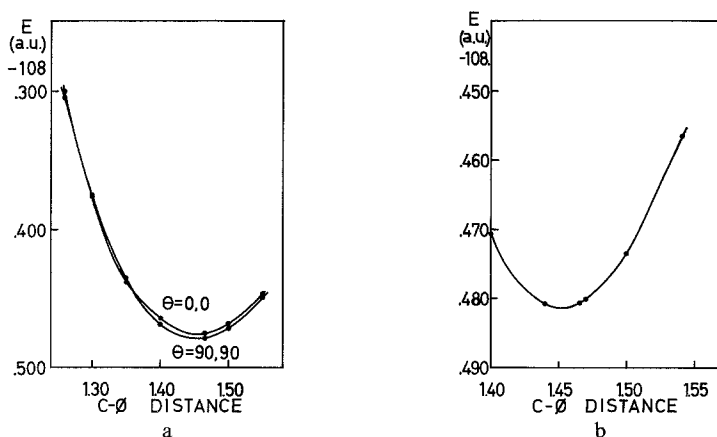
Fig. 4. Energy of a *trans-* and b *cis*-stilbene as a function of the C–Ø single bond length. For all phenyl rings, $\theta = 90°$

(upper curve) or perpendicular $(\theta = 90°)$ (lower curve) position. As before $\phi = 128°$. For the lower curve, the bond lengths are the same as those assumed in Fig. 2 while for the upper curve the C–Ø single bond length was chosen to be 1.455 Å. The reason for this choice will be given later. According to Fig. 3a the energy is almost constant for the region $\theta = 50°$ to $\theta = 90°$. Hence, apart from the small steric barrier in the planar form, the phenyl rings would be essentially free to rotate. The dependence of the energy of *cis*-stilbene upon the rotation of the phenyl rings is illustrated in Fig. 3b for the case where both phenyl rings are rotated by the same angle and in Fig. 3c for the case where one of the rings is held in a fixed position (at $\theta = 90°$ and $\theta = 60°$ respectively). All these curves record an essentially constant energy until steric hindrance is experienced. In order to find out whether this levelling off of the energy arises from the assumed constancy of the C–Ø bond length, the energy of the planar and perpendicular conformations was calculated for a number of different values of this distance (Fig. 4a). As appears from this diagram, both conformations have energy minima for the same value of the bond length, 1.455 Å. Moreover, the energy difference between the two conformations appears to be substantially constant within a certain interval about the equilibrium bond length. Thus, it seems unlikely that the adoption of different bond length values would seriously affect the conclusions drawn from Fig. 3a. Fig. 4b shows how the energy of *cis*-stilbene depends on the C–Ø distance. In this figure, $\theta = 90°$ for both phenyl rings, and $\phi = 128°$. The fact that the same equilibrium bond length 1.455 Å, is obtained as for the *trans*-conformation indicates that this value is effectively reliable. It is also in excellent agreement with the value given by Dewar [7], 1.465 Å.

As was discussed above, the size of the equilibrium angle ϕ (128°) is probably caused by the particular state of hybridization at the central carbon atoms. This indicates that the angle ψ might perhaps also be different from 120° in the lowest energy conformation. Fig. 2c shows the energy of perpendicular *trans*-stilbene as a function of the angle ψ. Minimum energy is obtained for $\psi = 118.7°$. However, compared to $\psi = 120°$, the energy is only lowered by 0.06 kcal/mole.
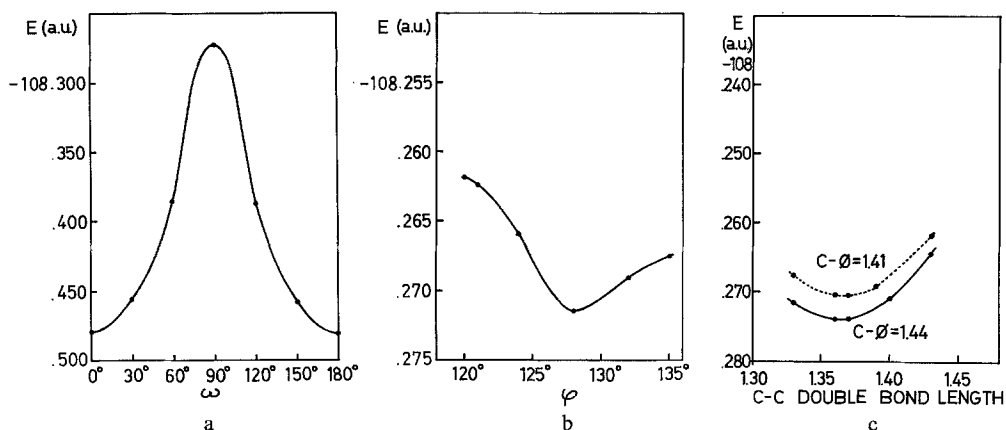
Fig. 5. Energy of stilbene in the *transition*-state of the rotational isomerization, a as a function of the angle ω, b as a function of the angle φ for one half of the molecule, c as a function of the central double bond distance. The upper curve represents the case that the C–Ø distance equals 1.54 Å, in the lower curve it equals 1.44 Å

Thus, in the majority of the calculations reported in this article, ψ was taken to be 120°.

From the above calculations the energies of the most probable conformations are found to be, for *trans*-stilbene −108.479 a.u. and for *cis*-stilbene −108.4815 a.u. If the vibrational energy change can be neglected we conclude that ΔE for the reaction *trans* → *cis* is −1.6 kcal/mole.

b) The Isomerization Barrier

Fig. 5a shows the energy variation when one half of the molecule is rotated in relation to the other half by an angle ω about the central C–C double bond. The usual values for the other angles and distances were adopted: $\phi = 128°$, $\theta = 90, 90$, C–C double bond length 1.33 Å, C–Ø bond length 1.44 Å.

In order to minimize the height of the rotational barrier, the angle φ for the right half of the molecule and the C–C double bond length were varied (Figs. 5b and c). As appears from Fig. 5b, minimum energy is still obtained for $\phi = 128°$. Thus in Fig. 5c, φ was held fixed at this value. The variation of the double bond distance was carried out for two different values of the C–Ø single bond length. The diagram shows that the lower energy is still obtained for a C–Ø single bond length of 1.44 Å, whereas the C–C double bond has the length 1.365 Å in this conformation. The stretching of the double bond at the top of the barrier is therefore negligible.

We conclude that the energy at the top of the barrier is −108.2740 a.u./mole which is 129 kcal/mole above that of the *trans*-equilibrium conformation. This value is about three times the experimental result of 42.8 kcal/mole [8]. It should be noted that Fischer and Kollmar obtained a similar discrepancy for force constants when they used the parametrization of the CNDO/2 method [9].

Discussion

According to the calculations reported above, the phenyl rings are practically free to rotate about the C–Ø, essentially single, bonds. Similar results have been obtained by CNDO calculations on analogous molecules such as N-benzylidene-aniline [10] and biphenyl [11], where, according to the calculations, the phenyl rings have a negligible rotational barrier in the *trans*-conformation apart from a more or less pronounced steric hindrance. In the *cis*-conformation the steric hindrance will, of course, play a more important part. In the case of N-benzylideneaniline the picture is somewhat complicated by the fact that the phenyl ring attached to the nitrogen atom is able to conjugate with the free electron pair of the nitrogen atom.

The picture outlined above deviates considerably from that usually accepted for the conformation of stilbene. It is usually assumed that the molecule has a strong preference for the planar conformation owing to a supposed gain in resonance energy obtained with this geometry. This view also gained support from the fact that, according to X-ray diffraction evidence [6, 12, 13], *trans*-stilbene and biphenyl crystallize as planar molecules. In the case of biphenyl, however, electron diffraction studies of the vapour state [14–16] as well as indirect evidence from ultraviolet spectroscopy [17] have revealed that biphenyl has a nonplanar conformation in the liquid and vapour states. It was concluded that the phenyl rings are rotated with respect to one another, the rotation angle being greatest in the vapour state. The conclusion that different equilibrium conformations are, in fact, possible in different states of aggregation makes it desirable to investigate whether a similar situation might be found in the case of stilbene. In any case, it seems obvious that the results of quantum chemical calculations on an isolated molecule should preferably be compared with vapour phase data and that too much significance should not be attached to crystallo-graphic and similar evidence. In this connection it should be remarked that the shape of the solution and vapour spectra of stilbene have led Suzuki (cf. Ref. [17], p. 313) to suggest that the most preferred conformation of *trans*-stilbene in the vapour state would, in fact, be non-planar.

The possibility that the *trans*-stilbene molecule might show a smaller or greater deviation from planarity is evidently dependent upon the relative magnitude of the delocalization energy in the planar conformation on the one hand and the steric interaction energy due to contact between hydrogen atoms and possibly other energy terms, on the other.

The present CNDO calculations show an energy maximum in the planar *trans*-conformation, Fig. 3a, which probably originates from steric interaction between hydrogen atoms 5 and 11 and 1 and 12 respectively. The virtual absence of other energy variations in Fig. 3a would then probably indicate, either that the CNDO method underestimates the change in the resonance energy of the π-electron system when the angles θ are varied or that this effect is obscured by other energy terms of a non-bonding type.

The fact that the CNDO/2 method yields a negligible energy change for the butadiene molecule when one half of the molecule is rotated in relation to the other half about the central single bond [18] seems to support the former

possibility. This proposal gains further support from the fact that the CNDO calculations give a lower energy for *cis*- than for *trans*-stilbene (by 1.6 kcal/mole) in direct opposition to Kistiakowsky's experimental measurements [8] according to which the *trans*-isomer has a lower energy than the *cis*-isomer by approx. 3 kcal/mole. Hence, the experimental results appear to indicate the existence of a resonance stabilization of the planar *trans*-conformation which is probably not correctly reproduced by the CNDO method. Kistiakowsky's value for the energy difference between the two isomers is based on a determination of the equilibrium between the *cis*-and *trans*-isomers using the formulae

$$-\Delta G^0 = R T \ln K,$$

$$\Delta H^0 = \Delta G^0 + T \Delta S^0,$$

and setting $\Delta S^0 = 0$ which is a reasonable assumption provided that both isomers have fairly rigid structures. In the range 320–341 °C Kistiakowsky found $K = [cis\text{-stilbene}]/[trans\text{-stilbene}] = 0.07$ which yields the figure $\Delta H = 3$ kcal/mole as already quoted. The existence of a resonance stabilization of the planar *trans*-conformation is further corroborated by the fact that higher values of K, corresponding to higher concentrations of the *cis*-isomer in the equilibrium mixtures is obtained with substituted stilbenes which for steric reasons are prevented from assuming a planar conformation. Thus for α-methylstilbene, the value obtained is $K = 0.5$ [19].

On the other hand, there is some evidence that the stabilization energy of the planar form is probably rather small. Thus, as pointed out by Dewar [7], the calculated (by the Pople method) and observed resonance energies are very close to those for two molecules of benzene (1.74 eV), while the lengths of the single and double bonds of the central part of the molecule correspond closely to those of ordinary polyenes.

Another indication as to the magnitude of the resonance energy may possibly be obtained from the corresponding figures for butadiene [20] and cyclohexadiene [21] which are only 3.5 kcal/mole and 1.8 kcal/mole, respectively, (as obtained from heats of hydrogenation).

Starting from a Hückel molecular orbital calculation [22] which yields the value 11 kcal/mole for the stabilizing energy of *trans*-stilbene in the planar state Adrian [23] has attempted a theoretical calculation of the energy difference between *cis*- and *trans*-stilbene. Assuming the twisting angle, θ, to be 30 to 40° for *cis*-stilbene and zero twisting for the *trans*-isomer he finds $\Delta H = 6$ kcal/mole which is about twice the experimental value quoted above. Although Adrian's method of estimating the functional dependence of the resonance and steric energies on the twisting angle uses a simplified theoretical argument it seems likely that the value for the resonance energy calculated by the HMO-method is too large. This is consistent with the well-known observation that the HMO-method often yields too high values for delocalization energies and sometimes even fails to differentiate between aromatic and non-aromatic compounds [7].

Thus, from the above argument it appears resonable to infer that the difference in delocalization energy between planar and perpendicular stilbene is probably only a few kilocalories and almost certainly less than the value predicted by the HMO-method.

In such a situation it cannot *a priori* be excluded that non-bonding forces of an attractive or repulsive origin such as were discussed by Fink and Allen [24, 25], by Allen [26] and by Parr *et al.* [27, 28] might have an important influence on the shape of the energy-*versus*-θ-curve. Such forces often reach a magnitude of a few kilocalories per mole as exemplified by the difference in energy between the staggered and eclipsed conformations of ethane which amounts to 2.928 kcal/mole [29]. It should also be remembered that a twisting of the phenyl rings nullifies the clear-cut distinction between π- and σ-electrons and causes the simple intuitive picture based on π-electron molecular orbital theory to break down.

The hope that the CNDO method would be able to cope with problems of this type having been partially dashed by the shortcomings of the method already referred to above, there exists, at present, no way of obtaining a detailed picture of the energy *vs.* θ dependence. Thus it cannot be decided whether *trans*-stilbene is planar or twisted. If $dE/d\theta$ is small, i.e. if the resonance energy decreases slowly with increasing θ for small θ, and if the steric interaction energy calculated by CNDO is at least qualitatively correct it cannot be excluded that the minimum energy conformation is twisted to some extent. The form of the UV-visible absorption spectra of *cis*- and *trans*-stilbene [30] and notably the great similarity between the solid and solution spectra of the *trans*-isomer [17, 31] would then point to the angle of twist being rather small.

However, the alleged differences between the solution and gas phase spectra of *trans*-stilbene as well as the inexplicably large differences between its spectra in different solvents [32] deserve careful consideration.

A final assessment of the relative efficacity of the CNDO method when dealing with problems of this type requires the use of a more direct method, e.g. gas phase electron diffraction.

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