

THE T_1 POTENTIAL ENERGY CURVE OF STILBENE: A SEMIEMPIRICAL STUDY WITH GEOMETRY OPTIMIZATION

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Summary

The sensitized photoisomerization in stilbene is governed by the potential energy curve along the torsional coordinate in the lowest triplet state (T_1). We have calculated this potential energy curve by the quantum chemistry force field (QCFF) method, which has the advantageous feature of allowing the relaxation of all the other coordinates while investigating the torsion. The calculated curve is rather flat with the absolute minimum close to the trans geometry.

The calculated vibrational modes of T_1 were compared with the few observed frequencies and the vibrational contributions to the free energy were estimated.

1. Introduction

Stilbene cis-trans photoisomerization has attracted the interest of many researchers. Most of the research has been focused on the direct photoisomerization which follows from the excitation on the lowest excited singlet S_1 , with the purpose of clarifying the mechanism of the process and of identifying the transient reaction intermediate [1 - 10]. The commonly accepted view is that direct photoisomerization occurs by the active involvement of a second excited singlet, S_2 , having a minimum at the twisted geometry [9, 10].

The present paper is concerned with the sensitized photoisomerization which results from the excitation on the lowest triplet T_1 which is usually accomplished by sensitization [11] (see, however, ref. 12). The ability of stilbene to undergo sensitized photoisomerization is related only to the shape of the potential energy curve of T_1 along the torsional coordinate (φ describes the torsion around the central C=C double bond) and no other triplet state is involved [13].

The experimental evidence shows that upon excitation on T_1 stilbene isomerizes with a quantum yield $\phi \approx 0.5$ [14]. Therefore during the lifetime of the T_1 triplet the molecule can move from the trans or the cis geometry

to the twisted geometry ($\varphi = 90^\circ$) from which it decays vertically to the ground state barrier and thereby isomerizes. Further observations on the azulene quenching of sensitized stilbene photoisomerization [15] and their kinetic analysis suggest that the trans and the twisted geometries are associated with shallow minima that are approximately degenerate and are possibly separated by a barrier of about 3 kcal mol⁻¹.

These conclusions have to some extent been revised in a subsequent study by the same group [16], based on a modified kinetic mechanism.

Theoretically, the occurrence of the sensitized photoisomerization is rationalized by the symmetry correlation diagram according to which the T₁ potential energy curve along φ is flat [9]. π -electron semiempirical calculations [17], which give details of the shape of this curve, reveal that at the cis geometry the T₁ energy reaches a maximum but cannot provide unambiguous information about the energy ordering of the trans and the twisted geometries or about the height of the barrier (if any) separating them. An important feature, however, has been neglected in all the calculations performed so far, namely the optimization of the other geometrical parameters in the calculation of the potential energy curve along φ . In fact the relaxation energy effect associated with geometric optimization has been shown to be as high as 10 kcal mol⁻¹ in retinal [18].

In this paper we report a calculation of the T₁ potential energy curve in which the optimization with respect to all the remaining coordinates is performed. The purpose is to obtain more reliable information on the shape, *i.e.* the existence and depth of minima, of this curve.

This investigation has been spurred by recent experimental work concerning the triplet energy transfer from anthracene and 9,10-dichloroanthracene to stilbene on the basis of which new details of the T₁ potential energy curves have been proposed [19].

In this work we have also calculated the vibrational frequency of stilbene in T₁ and monitored the change in the bonds and angles of the central moiety of the molecule as the torsion proceeds.

2. Details of the calculations

The calculations were performed by means of the quantum chemistry force field (QCFF) program of Warshel [20] which treats the π electrons explicitly by employing a Pariser-Parr-Pople hamiltonian and simulates the effects of the σ electrons by a suitably parametrized spring system. This program can locate the equilibrium geometries by the steepest-descent and the Newton-Raphson algorithms. The latter method, which makes use of the first and second derivatives of the potential energy surface, is more effective when the potential is harmonic or when the starting point is not too far from the minimum. The steepest-descent method, which employs the gradients only, is preferable in the other cases and it modifies the geometry by small steps. For this reason the geometry of the limiting cis and trans isomers was

optimized by 20 steepest-descent steps followed by 10 Newton-Raphson iterations. In the vicinity of $\varphi = 90^\circ$, we could not find a minimum in the potential energy surface by this procedure. The potential energy curve along φ was constructed, starting from the optimized trans geometry, by introducing step-by-step changes of 15° in the angle φ and then reoptimizing each geometry by not more than 10 steepest-descent cycles.

An examination of the reverse path over the cis-perp region (perp, perpendicular) showed substantial agreement with the trans-cis curve except in the close vicinity of the cis isomer. In this cis-perp region we adopted the energies obtained from the cis optimized geometry. The geometry parameters monitored (see Table 1) show a smooth transition between the trans-perp and the cis-perp values. The number of cycles adopted was found to be sufficient to adjust all the coordinates following each $15^\circ \Delta\varphi$ step, while modifying slightly the φ coordinate itself. For this reason, however, the calculated points do not show regular $15^\circ \Delta\varphi$ intervals.

The vibrational frequencies at the equilibrium trans geometry of the triplet are obtained by analytical construction of the force constant matrix with respect to mass-weighted cartesian coordinates followed by matrix diagonalization.

TABLE 1

Relaxation of four internal coordinates of stilbene in the T_1 state along φ

φ (deg)	R_1	R_2	α_1	α_2
0	1.4251	1.4198	124.52	118.82
9	1.4246	1.4219	124.47	118.82
17	1.4260	1.4212	124.38	118.68
27	1.4292	1.4198	124.35	118.42
43	1.4351	1.4181	123.93	118.13
54	1.4441	1.4141	123.93	117.66
65	1.4524	1.4111	123.91	117.32
75	1.4609	1.4075	123.88	117.01
80	1.4657	1.4056	123.86	116.87
101	1.4630	1.4047	123.95	116.75
106	1.4593	1.4061	124.10	116.82
109	1.4576	1.4065	124.20	116.63
118	1.4514	1.4090	124.30	116.65
130	1.4422	1.4145	125.06	116.20
142	1.4328	1.4178	128.20	114.78
149	1.4298	1.4201	128.83	114.58

$R_1 \equiv R(C_e-C_e)$; $R_2 \equiv R(C_e-\phi)$; $\alpha_1 \equiv C_e C_e \phi$; $\alpha_2 \equiv C_e C_e H$.

3. Results and discussion

The calculated T_1 energy curve, taking into account the relaxation of all the other coordinates, is displayed in Fig. 1(a). This energy curve appears to

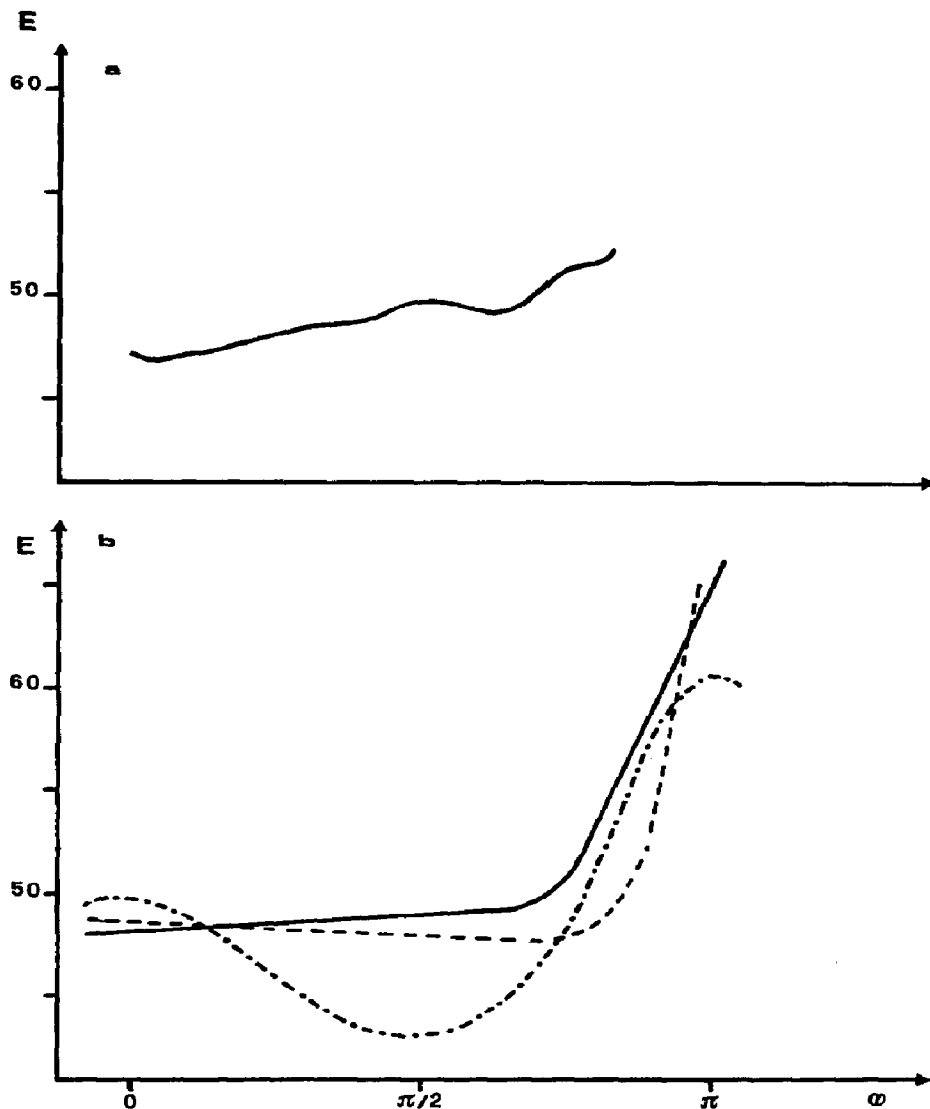


Fig. 1. (a) Calculated energy curve upon twisting about the central double bond in the T_1 state of stilbene (energy in kilocalories per mole). (b) ΔH (—) and ΔF (---) curves in the T_1 state of stilbene proposed in ref. 15; ···, ΔH curve proposed in ref. 19.

be essentially flat, in remarkable agreement with the results of the schematic symmetry correlation energy diagram [9]. The absolute minimum is found at the trans geometry while at the twisted geometry a very slight barrier ($E_b \approx 1.5 \text{ kcal mol}^{-1}$) is observed. A secondary, very shallow, minimum which appears at $\varphi = 110^\circ$ is considered to be physically meaningless because it cannot support a thermodynamically independent species. The cis isomer lies at a higher energy, but only 4 kcal mol^{-1} higher than the trans isomer. Such an energy difference is smaller than that found in previous calculations [17] and is related to the relaxation of all the geometrical parameters, which

is especially important at the crowded cis geometry. This smaller ΔE appears also to be in better agreement with the $T_1 \leftarrow S_0$ absorption spectra [21] which show that the cis and trans spectra fall in the same energy region, although the shape of absorption spectra is indicative of larger displacements between the equilibrium geometry of T_1 and S_0 of the cis form than of the trans form. (This is confirmed by the theoretically predicted equilibrium coordinates.)

The relaxation of four geometrical parameters pertinent to the ethylenic moiety along the torsional coordinate is shown in Table 1. The ethylenic bond R_1 lengthens by 0.04 Å on going from the quasi-planar trans or cis geometry to the twisted geometry. The ethylene-benzene bond on the contrary shortens by 0.015 Å under the same conditions. Both results are reasonable and agree with the notion that in the cis or the trans geometry stilbene is a unique π system while at the twisted geometry it corresponds to two non-interacting benzyl moieties. The ethylenic "in plane" angles $C_e C_e \phi$ and $C_e C_e H$ undergo a large change when moving towards the cis geometry in order to minimize the non-bonded interactions.

The equilibrium geometries of the trans and the cis isomers in the S_0 and S_1 states have been computed previously by the same method [21]. The presently calculated triplet values show, with respect to S_0 , a trend similar to the S_1 singlet, with small changes: the lengthening of the central (ethylenic) bond and the widening of the dihedral $\phi-C-C-\phi$ angle in the cis isomer are less pronounced than in the case of the singlet, but the changes in the central CCC and CCH angles are more pronounced than in the singlet.

The T_1 vibrational frequencies, at the absolute minimum of the trans geometry, have also been calculated and are reported in Table 2. Very scarce experimental data so far exist: the only resolved $T_1 \leftarrow S_0$ spectrum available [23] taken on crystalline *trans*-stilbene allows seven frequencies of T_1 to be extracted. These frequencies are given in parentheses in Table 2.

In particular, the B_g 308 cm^{-1} out-of-plane bending mode, which gives rise to the most intense false origin, can be identified. The closest calculated frequency corresponding to a B_g mode is 290 cm^{-1} , having the $C_e-\phi$ torsion as the main component. The totally symmetric modes with frequencies 1561 cm^{-1} , 1497 cm^{-1} and 637 cm^{-1} , however, can be assigned to the calculated modes having frequencies 1621 cm^{-1} , 1583 cm^{-1} and 701 cm^{-1} respectively. This assignment finds confirmation in the correlation between the S_1 and T_1 calculated modes and in the assignment of the S_1 frequencies. More ambiguous is the case of the modes observed at 1282 cm^{-1} , 898 cm^{-1} and 264 cm^{-1} , for which only a tentative assignment is given in Table 2.

We now wish to compare the calculated T_1 energy curve with that inferred from energy transfer experiments. The quenching of stilbene triplets by energy transfer with the formation of *trans*-stilbene and the efficiency of *trans*-stilbene as a vertical acceptor of triplet energy have led to the suggestion of a triplet energy curve with two shallow minima at the twisted and the trans geometries [11, 15, 24], designated p^* and t^* respectively (Fig. 1(b)).

TABLE 2

Calculated vibrational frequencies of normal modes for *trans*-stilbene (with the exception of CH stretches) in the first excited singlet state and in the first excited triplet state (the few experimental data available for the triplet are reported in parentheses)

Singlet calculated ^a	Triplet		Description
	Calculated	Observed ^b	
<i>Ag</i>			
1671	1621	(1561)	C—C st
1606	1583	(1497)	C—C st + C _e —C _e st
1566	1548		C—C st + C _e —C _e st + CCH bend
1523	1505		C—C st + CCH bend
1500	1475		C—C st + CCH bend
1460	1408		C—C st + CCH bend (ring)
1392	1382		C—C st + CCH bend
1321	1315		C _e C _e H bend
1264	1252	(1282)	C—C st + CCH bend (ring)
1177	1175		CCH bend
1155	1156		CCH bend
1086	1087		CCH bend
1041	1041		CCH bend + CCC bend
1036	1029		C—C st + CCC bend
915	913	(828)	CCCH bend + CCC bend
700	701	(637)	CCH bend + CCC bend
654	653		CCC bend
309	308	(264)	CCC bend
230	230		C _e —C _e — ϕ bend
<i>Bg</i>			
1012	1031		CCCH + CCCC + HCCH
1003	1025		HCCH + CCCH + CHCC
903	909		CCCH + CCCC + HCCH
834	821		CCCH + HCCH
800	793		CCCH + CCCC
715	725		CCCH + CHCC
603	620		Ring def
445	454		Ring def
401	407		Ring def
289	290	(308)	C _e — ϕ tor
131	136		C _e — ϕ tor
<i>Au</i>			
1006	1031		CCCH + CCCC
999	1025		CCCH + HCCH
906	910		HCCH + CCCC + CCCH
888	881		CCCH + HCCH
797	818		CCCH + HCCH
721	736		CCCH + CCCC
611	631		Ring def + C _e —C _e tor
469	478		Ring def + C _e —C _e tor
396	404		Ring def
238	246		CCCC + CCCH

(continued)

TABLE 2 (continued)

Singlet calculated ^a	Triplet		Description
	Calculated	Observed ^b	
55	58		C _e -φ tor + C _e -C _e tor
41	48		C _e -φ tor + C _e -C _e tor
<i>Bu</i>			
1662	1621		C _e -φ st
1581	1559		C-C st
1543	1514		C-C st + CCH bend
1535	1497		CCH bend
1484	1423		C _e C _e H bend
1396	1380		CCH bend (ring)
1377	1363		CCH bend
1306	1292		C-C st + C _e C _e H bend
1174	1172		CCH bend
1157	1156		CCH bend
1090	1090		CCH bend
1046	1043		CCC bend
1021	1029		C-C st + CCH bend
862	861		C-C st + CCH bend
668	667		CCC bend
593	591		C-C st + CCH bend
548	546		CCC bend
88	98		CCC bend + CCH bend

st, stretch; def, deformation; tor, torsion.

^aFrom ref. 22.

^bFrom ref. 23.

The latter was inferred to be at a lower enthalpy while p* was suggested to be at a lower free energy.

Recently [19], the interpretation of the temperature dependence of the quenching of anthracene triplets by stilbene has led to the modification of the previous energy diagram [15] and to the proposal of ³p* as the absolute minimum in the triplet enthalpy curve (see Fig. 1(b)). In order to make a comparison with the curves of "experimental" origin we calculated the vibrational contribution to the enthalpy and the free energy and added them to the electronic energies. Such calculations were performed for the trans, twisted and cis geometries for which we could obtain values of the free energy and the enthalpy. The vibrational enthalpy H_v and the free energy F_v were calculated by the relations [25]

$$H_v = \sum_i \hbar\omega_i \left[0.5 + \left\{ \exp\left(\frac{\hbar\omega_i}{kT}\right) - 1 \right\}^{-1} \right] \quad (1a)$$

$$F_v = kT \sum_i \ln \left\{ 1 - \exp\left(-\frac{\hbar\omega_i}{kT}\right) \right\} + \sum_i \frac{\hbar\omega_i}{2} \quad (1b)$$

where ω_i is the frequency of the i th mode, k is the Boltzmann constant and T is the temperature. The results obtained are reported in Table 3. The vibrational enthalpy value remains practically constant along the torsional coordinate: the largest enthalpy difference is 0.9 kcal mol⁻¹ which is considered to be of the same order of magnitude as the inaccuracy in the calculation. The highest value of the vibrational enthalpy is found close to the twisted geometry for $\varphi = 80^\circ$. The calculation could not be performed at 90° because no minimum is found there. The results of Table 3 indicate that the enthalpy (H) curve, obtained by adding $E + H_v$, has the absolute minimum at the trans geometry rather than at the twisted geometry. The vibrational free energy has a minimum 3 - 4 kcal mol⁻¹ deep near $\varphi = 90^\circ$.

TABLE 3

Vibrational enthalpy H and free energy F at selected trans, twisted and cis geometries

	0°	80°	109°	168°
H (kcal mol ⁻¹)	138.4	139.3	138.8	138.4
F (kcal mol ⁻¹)	126.8	123.0	125.6	127.2

Even though this result must be considered to be only qualitative, it clearly suggests a minimum at 90° for the total free energy (F) curve.

In a recent paper Saltiel *et al.* [19] have proposed an enthalpy curve with the minimum at the twisted geometry, on the basis of the temperature dependence of the rate constants for triplet excitation transfer from anthracene to stilbene. The present calculation does not support this feature of the enthalpy diagram, but, given the absence of a sizable barrier, it confirms the notion of only one triplet species. It is also interesting to note that the calculated diagram is in agreement with the curves proposed in an earlier work [15] by the same group on the basis of energy transfer kinetics.

In conclusion, we have calculated the potential energy in the lowest triplet state of stilbene as a function of the coordinate of torsion around the central C=C bond, taking into account the relaxation of all the other coordinates. The vibrational enthalpy and free energy correction have been estimated. The resulting curves have been discussed in the light of the empirical diagrams inferred from kinetic measurements. The triplet vibrational frequencies have been calculated and have been used to assign the few frequencies observed.

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References

- 1 J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton and O. C. Zafiriou, *Org. Photochem.*, **3** (1973) 1.
- 2 G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **62** (1940) 2973.
- 3 Th. Förster, *Z. Electrochem.*, **56** (1952) 716.
- 4 H. Dyke and D. S. McClure, *J. Chem. Phys.*, **66** (1962) 2486.
- 5 S. Malkin and E. Fischer, *J. Phys. Chem.*, **68** (1964) 1153.
- 6 J. Saltiel, E. D. Megarity and K. G. Kneipp, *J. Am. Chem. Soc.*, **88** (1966) 2336.
J. Saltiel, *J. Am. Chem. Soc.*, **90** (1968) 6394.
- 7 K. Yoshihara, A. Namiki, M. Sumitani and N. Nakashima, *J. Chem. Phys.*, **71** (1979) 2892.
M. Sumitani, N. Nakashima, K. Yoshihara and S. Nagakura, *Chem. Phys. Lett.*, **51** (1977) 183.
- 8 B. I. Green, R. M. Hochstrasser and R. B. Weisman, *Chem. Phys. Lett.*, **62** (1979) 427; *Chem. Phys.*, **48** (1980) 289.
F. E. Doany, E. J. Heilweil, R. Moore and R. M. Hochstrasser, *J. Chem. Phys.*, **76** (1982) 5632.
- 9 G. Orlandi and W. Siebrand, *Chem. Phys. Lett.*, **30** (1975) 352.
- 10 G. Orlandi, P. Palmieri and G. Poggi, *J. Am. Chem. Soc.*, **101** (1974) 3492.
P. Tavan and K. Schulten, *Chem. Phys. Lett.*, **56** (1979) 200.
- 11 G. S. Hammond, J. Saltiel, A. M. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, *J. Am. Chem. Soc.*, **86** (1964) 3197.
- 12 R. Benson and D. F. Williams, *J. Phys. Chem.*, **81** (1977) 215.
- 13 H. Suzuki, *Electronic Absorption Spectra and Geometry of Organic Molecules*, Academic Press, New York, 1967, Table 14.4.
- 14 H. A. Hammond, D. E. De Meyer and J. L. R. Williams, *J. Am. Chem. Soc.*, **91** (1969) 5180.
- 15 J. Saltiel, D. W.-L. Chang, E. D. Megarity, A. D. Rousseau, P. T. Shannon, B. Thomas and A. K. Vriarte, *Pure Appl. Chem.*, **41** (1975) 559.
- 16 J. Saltiel, A. D. Rousseau and B. Thomas, *J. Am. Chem. Soc.*, **105** (1983) 7631.
- 17 D. L. Beveridge and H. H. Jaffe, *J. Am. Chem. Soc.*, **87** (1965) 5340.
P. Borrell and H. H. Greenwood, *Proc. R. Soc., Ser. A*, **298** (1967) 453.
C.-H. Ting and D. S. McClure, *J. Chin. Chem. Soc.*, **18** (1971) 95.
F. Momicchioli, M. C. Bruni, I. Baraldi and G. R. Corradini, *J. Chem. Soc., Faraday Trans. II*, **70** (1974) 1325.
- 18 A. Warshel and M. Karplus, *J. Am. Chem. Soc.*, **96** (1974) 5677.
- 19 J. Saltiel, G. R. Marchand, E. Kirkor-Kaminska, W. K. Smothers, W. B. Muller and J. L. Charlton, *J. Am. Chem. Soc.*, **106** (1984) 3144.
- 20 A. Warshel and M. Karplus, *J. Am. Chem. Soc.*, **94** (1972) 5612.
A. Warshel and M. Levitt, *QCPE 247, Quantum Chemistry Program Exchange, Indiana University, 1974*.
- 21 A. Bylina and Z. R. Grabowski, *Trans. Faraday Soc.*, **65** (1969) 458.
- 22 A. Warshel, *J. Chem. Phys.*, **62** (1975) 214.
- 23 C.-H. Ting, *J. Chin. Chem. Soc.*, **17** (1970) 119.
- 24 V. Balzani, F. Bolletta and F. Scandola, *J. Am. Chem. Soc.*, **102** (1980) 2152.
G. Orlandi, S. Monti, F. Barigelletti and V. Balzani, *Chem. Phys.*, **52** (1980) 313.
- 25 R. Kubo, H. Ichimura, T. Usui and N. Hashitsume, *Statistical Mechanics*, North Holland, Amsterdam, 1978, pp. 80, 81.