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THE GEOMETRY OF HINDERED STILBENES IN THEIR GROUND AND EXCITED STATES

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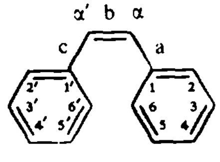
Abstract—The torsional angles about the 1-α single bond and about the α-α′ double bond in hindered stilbene derivatives were calculated for the ground and for the excited states. The calculated ground state geometries form a basis for a π-electron-SCF-LCAO-CI-MO calculation of the singlet excitation energies which agree accurately with the experimental values. The calculated potential curves for torsion about the 1-α bonds provide a qualitative explanation for the significant red shift and increase in intensity of the first singlet absorption band observed in these compounds at low temperatures.

IN THIS PUBLICATION we wish to describe results of a calculation of the geometries of hindered stilbene derivatives. The method used is based on a minimalization of the sum of the nonbonded interactions and strain energies, a procedure widely used in investigations of the ground state geometries of aliphatic[1] and aromatic[2,3] compounds. Our aims in the present work were twofold: (a) to explore the usefulness of this method for the ground and excited states of stilbenes, and (b) to obtain potential curves for certain molecular vibration modes in the ground and excited states. These curves are essential for a qualitative discussion of several special features of the electronic spectra of these compounds which were observed in previous investigations.[4]

The nonbonded interaction energies were calculated in the present work from the exp-6 interatomic potential of Williams.[5] The calculated ground state geometries resulting from the minimalization procedure were the input for a π electron MO calculation of the electronic excitation energies. The calculated excitation energies were in turn compared with the experimental values. The comparison between the calculated and the experimental energies served as an independent criterion for the evaluation of the accuracy of the geometry calculation procedure. In this respect the present approach to the calculation of transition energies in hindered stilbenes differs from the approach adopted by other authors,[6,7] who have used molecular geometry as an additional variable parameter in order to obtain agreement with the experiment. The relative success of the present geometry calculation scheme indicates that the Williams potential functions (which were derived from crystal packing studies in aromatics for large interatomic distances) have definite value for describing nonbonded interactions at small interatomic distances such as are encountered in molecular conformation investigations.

Computation method

For the present purpose we were interested only in approximate geometries of *cis* stilbene and of both *trans* and *cis* isomers variously substituted at one or more of the α,α′, 2,2′, 6 and 6′ positions. Therefore we limited the number of variable internal coordinates to the three most significant, e.g. the three twist angles about bonds 1-α, α-α′, and 1′-α′, both in the *trans* and *cis* isomers. The justification for this choice of variables is twofold: (a) changes in internal coordinates of atoms 2,3,4 (and 2′,3′,4′) in the *cis* isomers and of atoms 3,4,5 (and 3′,4′, and 5′) in the *trans* molecules do not affect the type of steric hindrance discussed here.



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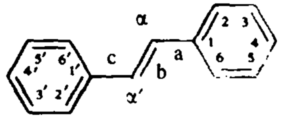

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Therefore these coordinates retained their assumed equilibrium values. (b) The restoring force constants for distortions of coordinates of other atoms (*cf.* ref. 2) are considered to be large enough so that the resulting distortions would be negligible, were the corresponding coordinates included in the minimalization scheme. The potential barrier (E_ϕ) for bond twisting (by angle ϕ) used in the present work is of the form

$$E_\phi = \tfrac{1}{2} K_\phi (1 + \cos 2\phi) \tag{1}$$

The force constant K_ϕ for this distortion was assumed to be proportional to the π-bond order P of the given bond:

$$K_\phi = K_{C=C} \cdot P \tag{2}$$

$K_{C=C}$ is the torsional potential barrier of an isolated double bond. The value adopted in the present work, $K_{C=C} = 40$ Kcal/mole was obtained in isomerization studies.[8] Eq. 1 and 2 are especially convenient for the calculation of torsional barriers in the excited state from the corresponding bond orders obtained from π-electrons MO calculations.

The strain forces resulting from bond torsion are assumed to act against the non-bonded interactions due to steric hindrance (at short atomic distances) in a way that a geometry is obtained for which the sum of the energy terms due to nonbonded interactions and to the strain energies is minimized.

The nonbonded interaction between atoms i and j is given by Eq. (3)[5]

$$E_{NB} = A_{ij} r_{ij}^{-6} + B_{ij} \exp(-C_{ij} r_{ij}) \tag{3}$$

The values of the parameters A, B, and C depend only on the atom pair ij. The values adopted in the present study (Set IV in ref. 5) are listed in Table 1.

TABLE 1. PARAMETERS FOR NONBONDED POTENTIAL[a]

Atom pair	A	B	C
C---C	−535	74,460	3·6
C---H	−139	9411	3·67
H---H	−36	4000	3·74

[a] Units adjusted so that E_{NB} is in Kcal/mole, r_{ij} in Å: values are taken from ref. 5.

The electronic transition energies were calculated by the Pariser–Parr–Pople method.[9] All singly excited configuration interactions were included. The resonance integrals β_{ij} were calculated by the "variable β" method of Nishimoto and Forster.[10] For the present series of molecules we chose to use the parameters optimized for benzene derivatives (P_{ij} are the bond orders)

$$\beta_{ij} = -0{\cdot}51\,P_{ij} - 2{\cdot}04 \tag{4}$$

The core repulsion integrals (γ_{ij}) were calculated according to the Nishimoto–Mataga approximation, Eq. 5 and 6,[11]

$$\gamma_{ij} = 14{\cdot}397/(a_{ij} + r_{ij}) \tag{5}$$

$$a_{ij} = 7{\cdot}198(1/r_{ii} + 1/r_{jj}) \tag{6}$$

According to the "variable β" method[10] all the distances for the MO calculation are taken equal to 1·40 Å. However in the nuclear conformation calculation the C—C bond distances were calculated (for ground and excited states) according to the bond length-bond order equation of Coulson and Golebiewski.[12]

$$r_{ij} = -0{\cdot}18\,P_{ij} + 1{\cdot}517 \tag{7}$$

In this calculation the C—H bond length was taken as 1·097 Å. All bond angles were assumed equal to 120° except the 1-α-α′ and 1′-α′-α bond angles which were assumed equal to 128°, the experimental value in *trans*-stilbene.[13]

The effects of Me groups on the electronic energies have been neglected.

RESULTS AND DISCUSSION

The compounds examined in the present study will be denoted subsequently by the numerals given in parentheses, as follows: *trans*-stilbene (**1**), *cis*-stilbene (**2**), *trans*-3,5,3′,5′-tetramethylstilbene (**3**), *cis*-3,5,3′,5′-tetramethylstilbene (**4**), *trans*-α,α′-dimethylstilbene (**5**), *cis*-α,α′-dimethylstilbene (**6**), *trans*-2,4,6,2′,4′,6′-hexamethylstilbene (**7**), *cis*-2,4,6,2′,4′,6′-hexamethylstilbene (**8**), *trans*-α-methylstilbene (**9**), *cis*-α-methylstilbene (**10**), *trans*-2,4,6-trimethylstilbene (**11**), *cis*-2,4,6-trimethylstilbene (**12**), and 1,2-diphenylcyclopentene (**13**).

The minimum energy torsional angles ϕ about the central bonds 1-α, α-α′ and 1′-α′ denoted subsequently by subscripts *a*, *b*, and *c* and the corresponding π-bond orders *P*, both for the ground state and for the first excited singlet state are listed in Table 2.

The torsional angles ϕ listed in Table 2 are defined through the dihedral angles ϕ^{d}_{ABCD} (measured clockwise between planes common to atoms A, B, C, and atoms B, C, D, and observed along BC in the direction from B to C). For the *cis* compounds (*cf.* formula I) $\phi_a = 180 - \phi^{d}_{21\alpha\alpha'}$, $\phi_c = 180 - \phi^{d}_{\alpha\alpha'1'2'}$, $\phi_b = 360 - \phi^{d}_{1\alpha\alpha'1'}$. For the *trans* compounds (*cf.* formula II) $\phi_a = 180 - \phi^{d}_{21\alpha\alpha'}$, $\phi_c = -180 + \phi^{d}_{\alpha\alpha'1',2'}$ and $\phi_b = 180 + \phi^{d}_{1\alpha\alpha'1'}$, with the exception of **7** where $\phi_c = 180 - \phi^{d}_{\alpha\alpha'1'2'}$. A few typical potential curves for the twisting modes about bonds *a* and *c* are given in Fig 1 (ground state) and in Fig 2 (first excited singlet state). For *cis* stilbene (**2**) potential curves are also given for several values of ϕ_b. Both in Fig. 1 and 2 the energy coordinates represent the sum of the nonbonded and of the strain energies. In most cases the poten-

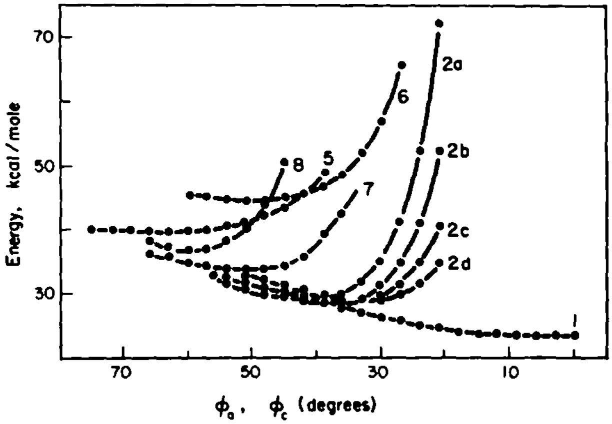

FIG 1. Sum of strain and nonbonded energies *vs.* torsional angles ϕ_a and ϕ_c in the electronic ground states of 2, 5, 6, 7, and 8. For 2 curves are given for the following values of ϕ_b: a – 0°, b – 5°, c – 10° and d – 15°

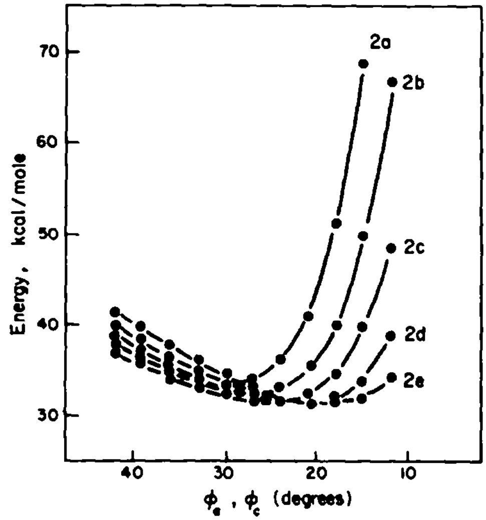

FIG 2. Sum of strain and nonbonded energies *vs.* ϕ_a and ϕ_c in the first excited singlet state of *cis* stilbene (2), for the following values of ϕ_b: a – 10°, b – 15°, c – 25° and d – 30°

tial curves are very shallow in the minimum region. For this reason and because of the approximate character of the present procedure we report the angles ϕ_a, ϕ_b, and ϕ_c rounded to the nearest 5 or 10 degrees. For unhindered molecules (1 or 3) the potential curves are especially shallow and the uncertainty in the minimum energy values is even larger, 0–15°. Values obtained in recent crystallographic studies for angle ϕ_a (or ϕ_c) in sterically similar surroundings fall within the range calculated in the present work. In *p*-chlorocinnamide ϕ_a is 14·2°,[15a] in *p*-methoxychalone –4·5°,[15b] and in 1-phenyl-4-(2,6-dichlorophenyl)butadiene –14°.[15c]

The transition energies to the lowest excited singlets and the oscillator strengths

TABLE 2. CALCULATED TWIST ANGLES AND π-BOND ORDERS[a, b]

	Ground state						First excited singlet state					
												P_c
1	0–15	0	0–15	0·335	0·890	0·335	0–5	0	0–5	0·555	0·536	0·555
2	35–40	5	35–40	0·271	0·927	0·271	25–30	20	25–30	0·506	0·571	0·506
3	0–15	0	0–15	0·335	0·890	0·335	0	0	0	0·555	0·536	0·555
4	35–40	5	35–40	0·271	0·927	0·271	25–30	20	25–30	0·506	0·571	0·506
5	60–65	0	60–65	0·158	0·975	0·158	50–55	0	50–55	0·394	0·671	0·394
6	50–55	0	50–55	0·207	0·957	0·207	40–45	5	40–45	0·451	0·618	0·451
7	50–55	0	50–55	0·207	0·957	0·207	45–50	0	45–50	0·447	0·622	0·447
8	55–60	0	55–60	0·184	0·966	0·184	50–55	5	50–55	0·428	0·639	0·428
9	25–30	0	55–60	0·292	0·939	0·188	20–25	5	45–50	0·543	0·589	0·399
10	50–55	5	25–30	0·214	0·940	0·295	35–40	15–20	20–25	0·433	0·578	0·542
11	50–55	0	0	0·214	0·950	0·324	45–50	0	0	0·425	0·569	0·567
12	60–65	5	25–30	0·165	0·943	0·291	55–60	15–20	15–20	0·365	0·590	0·550
13	40–45	0	40–45	0·251	0·937	0·251	35–40	0	35–40	0·489	0·585	0·489

[a] Angles are given in degrees.

[b] *Cf.* text for definitions of ϕ_a, ϕ_b, and ϕ_c.

obtained in the present calculation are listed in Table 3, together with the experimental vertical excitation energies and extinction coefficients.

The overall agreement between the calculated and the experimental singlet excitation energies obtained by this method is rather good. As the Nishimito–Forster parametrization reproduces quite well the experimental excitation energies of

TABLE 3. COMPARISON OF CALCULATED AND EXPERIMENTAL SINGLET EXCITATION ENERGIES AND INTENSITIES

Compound	E[a]	f[b]	E[c]	ε[d]
1	4·102	1·339	4·202	27,950 f = 0·739
	5·843	0·600	5·427	16,500
	6·35	0·556	6·160	23,900
2	4·438	0·645	4·428	10,450 f = 0·323
	5·793	0·15	5·535	24,400
5	5·323	0·841	5·095	12,270
6	4·901	0·57	4·920	8880
7	4·966	0·986	4·717	16,000
8	5·082	0·538	4·793	15,100
9	4·721	1·08	4·553	21,100
10	4·554	0·637	4·654	9340
11	4·527	1·16	4·428	22,000
12	4·736	0·627	4·797	13,600
13	4·581	0·619	4·592	12,100

[a] Calculated singlet excitation energies, in ev.

[b] Calculated oscillator strength.

[c] Experimental singlet excitation energies in ev.

[d] Experimental extinction coefficients.

[e] Experimental values are taken from Suzuki,[7b] with the exception of values for 8, 11 and 12, taken from ref. 4b, and for 13.[14]

aromatics, the agreement observed presently is a good indication to the accuracy of the calculated twist angles. As shown in Table 4 our values for the ϕ_a and ϕ_c twist angles are (for the symmetric compounds) quite similar to the estimates of Suzuki,[7b] which were obtained as additional parameters introduced for the optimization of his MO calculation. For the unsymmetrically substituted stilbenes (i.e. **9** and **10**) the values reported by Suzuki are only average twist angles.

Table 4. Comparison of ground state twist angles values obtained by different methods

Compound	Twist angles ϕ_a and ϕ_b Present work	Ref. 6	Ref. 7b
1	0–15	0	0
2	35–40	30	28
5	60–65		58
6	50–55		51·5
7	50–55		54·5
9	25–30, 35–40		34·5
10	50–55, 25–30		40·0

The low temperature red shift of the first absorption band in stilbene

We shall presently apply the results described in the previous section for analyzing the remarkable effects of cooling on the absorption spectra of stilbenes in hydrocarbons solutions. Previous work[4a,b] has shown that the first absorption band of stilbenes (especially of the sterically hindered molecules) undergoes a striking enhancement of intensity and a large red shift on lowering the temperature from *ca.* 300°K to about 77°K. A few typical examples of this effect are shown in Fig 3 (a, b, c, and d).[16a] Measurements of the thermal expansion of solvents used in the present study over the temperature range 300°K to 77°K yield approximate values of *ca.* 1% volume change per 10°K temperature increment.[16b] Thus the large increase in the intensity of the first absorption bands (Table 5) cannot be attributed to the volume shrinkage of the solvent which amounts to *ca.* 20% for cooling from 300° to about 77°K.

Table 5. Changes in intensity of first absorption band in stilbenes $(I/I_0)^a$ and red shifts ($\Delta\lambda$, in mμ) produced by cooling to low temperatures T

Compound	T, °K	I/I_0	$(I/I_0)^b$	$\Delta\lambda$
1	96	1·6	1·4	6[c]
2	85	1·6	1·4	11[d]
5	89	2·1	1·9	8[c]
7	87	2·1	1·9	20[c]

[a] Ratio of areas of the absorption bands. For **2**, **5**, and **8**, I/I_0 is the ratio of the long wavelength half band areas A/B (*cf.* Fig 3b).

[b] Intensities ratio corrected for solvent contraction.

[c] Methylcyclohexane (MCH)—methylcyclopentane (MCP) 1:1 by volume.

[d] MCH–isohexane (IH) 2:1.

Similar effects are observed for other aromatic compounds with essential single bonds such as biphenyl.

In our discussion we shall first consider the batochromic effect of cooling. We wish

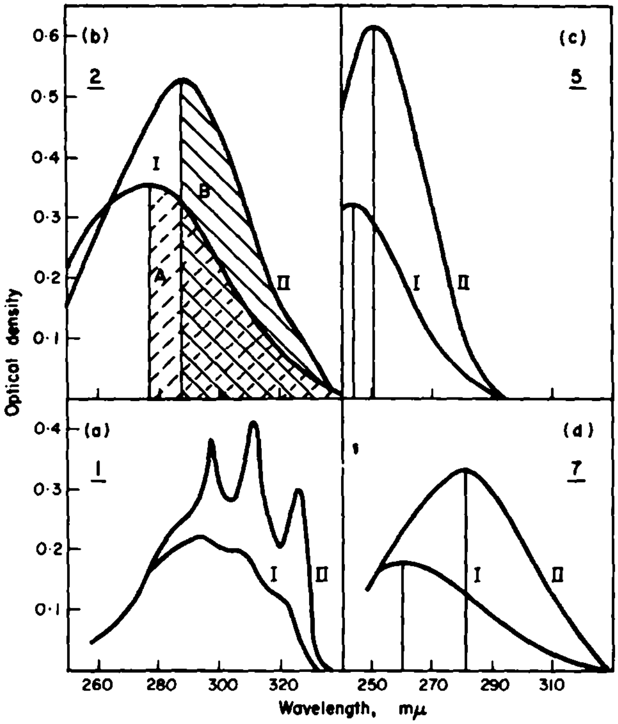

FIG 3. Absorption spectra of stilbenes in solution at 300°K and at low temperatures: (a) 1, 2 mg/l, in MCH/MCP, (b) 2, 10 mg/l in MCH/IH, (c) 5, 11 mg/l in MCH/MCP, (d) 7, 3·5 mg/l in MCH/MCP. In a–d I refers to spectra recorded at 300°K and II to the low temperature spectra (see Table 5)

to suggest that this effect is closely connected with the electronic ground state normal modes of vibrations approximately described as torsional vibrations about the 1-α and 1'-α' single bonds. These are low frequency modes[4a] and are therefore excited thermally at room temperature but are in their zero level at low temperatures.[17]

We may consider these torsional vibrations as vibrations of an asymmetric oscillator whose potential is approximately given by the curves of Fig 1 and 2. Then the probability distribution functions for the zero and the first level of such an oscillator assuming a classical frequency of 200 cm^{-1},[4a, 18, 19] may be described as in Fig 4.[20] (This model is valid in particular for 2 and 13). The main conclusion from such an entirely qualitative description is that on cooling from 300° to 77°K the population of the first level drops to about zero. Therefore the maximum probability twist angle value shifts from the left hand maximum of the 1st level to a *lower value*, proper to the zero level. In Fig 4 this decrease amounts to *ca.* 5°. The effect of such a change of the twist angle on the excitation spectrum may be estimated from the curve of Fig 5. A 5° decrease in the twist angle value results in a decrease of *ca.* 0·15 ev in excitation for the case of a molecule with an initial twist angle of *ca.* 40° about the single bond. This change corresponds to a low temperature red shift of *ca.* 9 mμ for molecules such as 2 and 13 in agreement with the values reported in Table 5.

We shall next consider the strong increase in intensity of the long wavelength bands

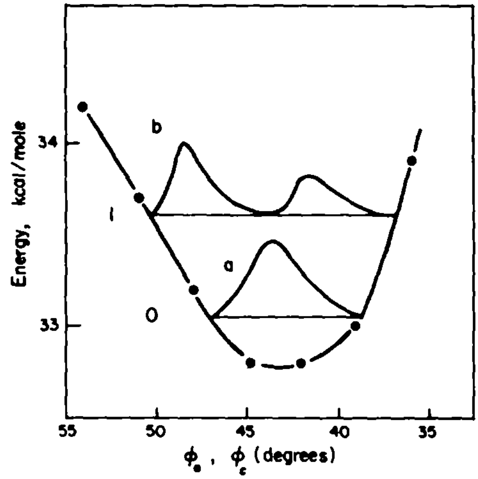

FIG 4. Potential curve of an asymmetric oscillator for torsional vibration in stilbenes (schematic). Curves a and b are respectively the probability distribution functions for the zero and first levels

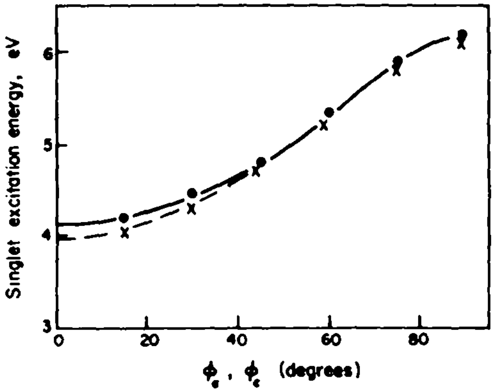

FIG 5. First singlet excitation energies as functions of twist angles of single bonds, ϕ_a and ϕ_c, in *trans* (●) and *cis* (X) stilbenes

at low temperatures (Fig 3 and Table 5). The π-electron LCAO-MO calculation indicates that this effect cannot be attributed to an increase of the oscillator strength (f) for the transition, due to a decrease of the maximum probability single bond twist angles. Thus in the case of *cis* stilbene, a much larger decrease in ϕ_a (and ϕ_c) results in an increase in f much too small to account for the effect ($\phi_a = 0°$, $f = 0{\cdot}664$; $\phi_a = 40°$, $f = 0{\cdot}619$).

However, the low temperature intensity enhancement can be readily explained by considerations based on the Franck–Condon (F.C.) factors for electronic transitions.* Table 2 indicates that the bond orders of the 1-α′ bonds and the corresponding twist angles (ϕ_a and ϕ_c) change considerably on excitation. Therefore the totally symmetric normal mode which is mainly composed of torsional vibration (τ) about the 1-α

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* For practical details and review of recent literature see ref. 21.

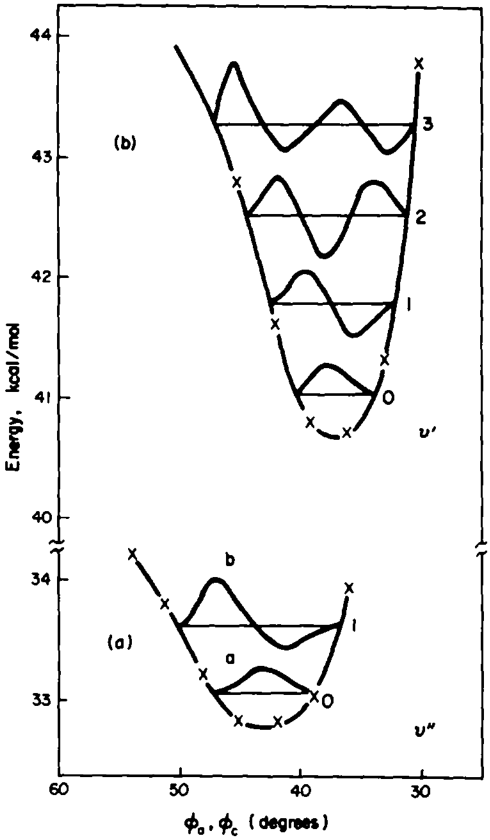

FIG 6. Potential curves for torsion about single bond 1-α in diphenylcyclopentene for ground (A) and excited (B) states. Horizontal lines represent the vibrational states. The corresponding wave functions are represented schematically

bond will be excited by the electronic transition.[21] For this mode the F.C. factor is expected to be much larger if the lower state (in the electronic ground state) is the zero level of τ, as it is the case at low temperatures.[22] The situtation to be expected is described schematically in Fig 6 (A and B), for the case of diphenylcyclopentene. The potentials for the lower and upper states are those that have been calculated in the present study. The vertical transitions ($v'' = 1 \rightarrow v' = 3$ or 4) at *ca.* 300°K should according to general considerations[22] be weaker than the low temperature transition ($v'' = 0 \rightarrow v' = 0$, 1 and 2).

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