221. *Theoretical Considerations Relating Spectra to Steric Factors in Hindered Stilbenes.*

By H. H. Jaffé and Milton Orchin.

Steric crowding in hindered *trans*- and *cis*-stilbene is more effectively relieved by twisting of the phenyl–ethylene single bonds than by twisting of the ethylenic linkage. Schematic ground- and excited-state diagrams of potential energy as a function of (*a*) the angle of twist around the exocyclic single bonds and double bond, and (*b*) the internuclear distance between the carbon atoms involved in these bonds are constructed. Analysis of these approximate diagrams in terms of the Franck–Condon principle leads to conclusions consistent with the observed hypochromic effect exhibited by both slightly hindered and moderately hindered stilbenes. With moderately hindered stilbenes, an additional contribution to the hypochromic effect arises from a reduced transition moment, as demonstrated by crude molecular orbital calculations. Such calculations of the bond orders in the ground and the excited states, and comparison with known bond angles and bond lengths in the ground state, indicate that the bonds involved do not change greatly on excitation. Calculation of the π-electron energies in the ground and the excited state of a moderately hindered stilbene shows that the molecular orbitals of the hindered molecule are compressed in both states relative to the planar model and thus the energy required for the long-wavelength $N \longrightarrow V$ transition from π to π^* is greater for the hindered model, in accordance with the observed hypsochromic effect. Application of the Franck–Condon principle alone would not explain the hypsochromic effect. The treatment is generalized to apply to other conjugated systems where there is hindrance to coplanarity around a single bond.

The ultraviolet absorption spectra of conjugated organic compounds differ from those expected for a planar model when the molecule is sufficiently crowded to render coplanarity of the conjugated atoms difficult or impossible. The degree of deviation from the expected spectrum seems to increase with the degree of steric crowding, and on this basis, three types of behaviour of the longest-wavelength band have frequently been distinguished:[1] (1) Slight crowding, the spectroscopic result of which is a hypochromic effect only. (2) Moderate crowding, resulting in both a hypochromic effect and a hypsochromic shift. (3) Severe crowding, resulting in complete steric inhibition of resonance, and giving rise to the cumulative spectra of the two isolated chromophores. The last type of steric effect is well understood, and will not be discussed further here.

The first two types of steric effect have been observed for many classes of compound and have been often separately discussed. A more systematic and unified examination of these cases appears desirable and will be attempted in the present paper. In order to highlight the problems involved, spectra of the hindered stilbenes will be examined first, and the arguments will then be generalized.

STILBENE

Stilbene is chosen as the special example for study because its spectrum and those of its derivatives [2] have been studied in detail,[3,4] and because stilbene's symmetry makes the

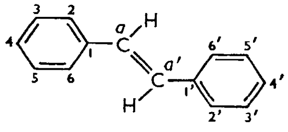
---

[1] Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1949, 1890; Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, **73**, 1403; Ingraham in " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, New York, 1956, p. 484.

[2] Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, *A*, **241**, 147.

[3] Beale and Roe, *J. Amer. Chem. Soc.*, 1952, **74**, 2302.

[4] *Idem, J.*, 1953, 2755.



treatment particularly attractive. Planar *trans*-stilbene will be considered as the unhindered reference molecule, and steric hindrance will be assumed to be introduced either by substitution in one or more of the *a*-, *a*′-, 2-, 6-, 2′-, and 6′-positions, or by conversion of the *trans*- into the *cis*-compound.

In ethanol *trans*-stilbene absorbs at 295·5 mμ with $\varepsilon_{\text{max.}}$ = 29,000, while *cis*-stilbene absorbs [3] at 280 mμ with $\varepsilon_{\text{max.}}$ = 10,450; the corresponding data for some substituted derivatives are shown in Table 1.[2] Although vibrations distorting planarity occur, the ground state of *trans*-stilbene is undoubtedly planar and the potential-energy minimum corresponds to the planar conformation. Steric repulsion of the *ortho*-hydrogen atoms, however, probably inhibits *cis*-stilbene from assuming a planar conformation, or at least makes this conformation energetically less favourable than a twisted one. The same repulsion also must lead to a distortion of other molecular parameters. Similarly, repulsion between a substituent in the 2(or 2′)-position and the hydrogen attached to carbon atom *a* (or *a*′), and particularly repulsion between a substituent in the 6(or 6′)-position and the hydrogen attached to *a*′(or *a*) leads to deviations from planarity and to distortions of other molecular dimensions.

TABLE 1. *Spectra of substituted stilbenes.*[2]

Substituent	Long-wavelength band $\lambda_{\text{max.}}$ (mμ)	$10^{-3}\,\varepsilon$	Substituent	Long-wavelength band $\lambda_{\text{max.}}$ (mμ)	$10^{-3}\,\varepsilon$
4-NMe$_2$	346	30·8	4-NMe$_2$-2′,4′,6′-Me$_3$	310	27·0
4-NMe$_2$-2′-Me	343	26·5	4-NMe$_2$-2,2′-Me$_2$	338	21·3
4-NMe$_2$-2′-Et	338	25·6	4-NMe$_2$-4′-Me	345	31·2
4-NMe$_2$-2′-Pr$^{\text{n}}$	333	23·6	4-Cl-4′-NMe$_2$	355	31·4
4-NMe$_2$-2′-Pr$^{\text{i}}$	330	26·0	2-Cl-4′-NMe$_2$	356	30·3
4-NMe$_2$-2′,5′-Me$_2$	338	24·3	4-NMe$_2$-*aa*′-Et$_2$	263	17·6
4-NMe$_2$-2′,5′-Pr$^{\text{i}}_2$	345	28·2	2,4,6-Me$_3$	282	18·9
4-NMe$_2$-2′6′-Me$_2$	309	25·1	2,4,6,2′,4′,6′-Me$_3$	264	8·3

In order to be able to discuss these steric effects systematically, it will be necessary first to consider which of all the many possible deformations, corresponding in all to the 72 fundamental vibrations ($3n - 6$) of stilbene, are likely to be involved in the relief of steric strain; next, the potential-energy diagrams for each of the deformations considered of interest will be constructed and used to examine the importance of the Franck–Condon principle; and finally a total-energy diagram will be constructed on the basis of these discussions and of rough molecular-orbital calculations.

Examination of models of hindered stilbene derivatives suggests that the following distortions of *trans*-stilbene should be considered: (*a*) Twisting about the *a*–1 (and *a*′–1′) bond. (*b*) Twisting about the *a*–*a*′ bond. (*c*) Stretching of the *a*–*a*′ bond. (*d*) Stretching of the *a*–1 bond (and *a*′–1′ bond). (*e*) In-plane deformation of the 1–*a*–*a*′ (and *a*–*a*′–1′) angle. (*f*) Distortion of bond distances and angles at the 2-, 2′-, and 6-, 6′-atoms, and of the *a*-H and *a*′-H bonds. These distortions (*f*) are unlikely to make an important contribution, and, even if they do, are not likely to affect the spectra seriously, and hence will be ignored hereafter.

Although the twisting modes (*a*) and (*b*) do not affect the σ-electron skeleton, the energetically inexpensive small twists tend to decrease rapidly the interaction between repelling atoms. Accordingly, these two are probably the most important modes. Of the two modes, twisting about the *a*–1 bond with a relatively low bond order, and the fact that there are two such bonds, make twisting around the single bonds more favourable than twisting about the *a*–*a*′ bond.

Stretching of the *a*–*a*′ bond, which, at 1·33 Å has about the length of a normal double bond,[5] produces an increase in σ-bond energy, and a decrease in π-electron energy; this mode is not as effective in relieving strain, but probably is involved to some extent. The

---

[5] Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568.

a–1 bond length [5] is 1·44 Å, just slightly shorter than recent estimates [6] of sp^2–sp^2 single-bond lengths of 1·48 Å; accordingly the decrease in π-electron energy on stretching of the *a*–1 bond is accompanied by little or no increase in σ-bond energy. Hence *a*–1 stretching is probably less important than the previous three deformations.

Bending of the 1–*a*–*a*′ angle undoubtedly occurs, since even in *trans*-stilbene this angle measures 133°.[5] However, the angle should have no effect on the π-electron system, and should not change appreciably during excitation, and hence is of no interest spectroscopically.

The Twisting Modes.—In constructing the potential energy curves for the twisting modes (*a*) and (*b*) the unhindered molecule will be considered first. Since, at equilibrium the state of the molecule is reasonably assumed to be planar, the ground-state curves must have minima for $\theta_{aa'} = 0°$ and $\theta_{a1} = 0°$. The total π-electron energy ($\mathcal{E}$), and hence the resonance energy of the molecule, will decrease as either of these angles increases. It can readily be shown that the resonance integral β of the *p*π-orbitals of the atoms forming a bond is proportional to cos θ, where θ is the angle by which the axes of the *p*π-orbitals of the two atoms are twisted with respect to one another. Since a change $\Delta\mathcal{E}$ of $\mathcal{E}$ caused by a change $\partial\beta_{rs}$ in the resonance integral β_{rs} of a bond rs with bond order p_{rs} can be expressed [7] as:

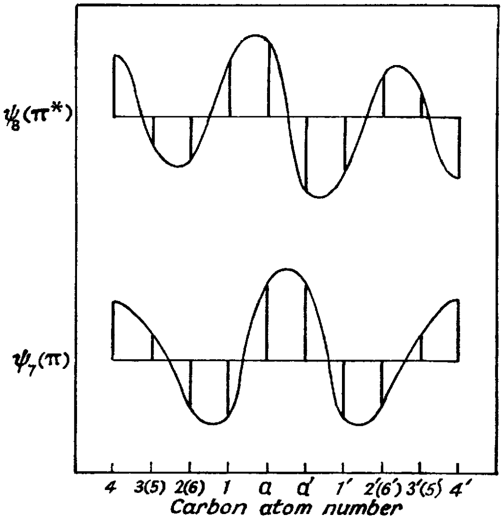
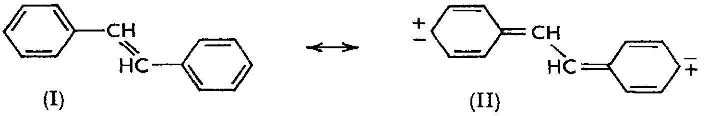


FIG. 1. *Graphic representation of the molecular orbitals* $\psi_7(\pi)$ *and* $\psi_8(\pi^*)$, *showing the amplitude of the wave functions (and the locations of the nodes) used in the calculation of bond orders.*

$$\Delta\mathcal{E} = p_{rs}\partial\beta_{rs}$$

it is apparent that the potential-energy curve should have the shape of a cos θ curve, and that the depth of the minimum, and hence the steepness of the curve, should be proportional to the appropriate *p*. Examination of the highest occupied (π) and the lowest unoccupied (π*) molecular orbitals of stilbene, graphically represented in Fig. 1,[8] shows that π has no node between atoms *a* and *a*′, but that π* does have a node between these atoms, while the situation is just reversed for atoms 1 and *a*, and 1′ and *a*′. Consequently, π makes a positive contribution to the bond order ($p_{aa'}$) of the *a*–*a*′ bond and a negative contribution



(I) (II)

---

[6] *E.g.*, Coulson, *Chem. Soc. Special Publ.*, No. 12, 1958, pp. 89 *et seq.*

[7] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.

[8] These are constructed on the basis of the free-electron model; cf. Jaffé, *J. Chem. Phys.*, 1953, **21**, 1287.

to p_{a1} of the 1–a bond. Similarly, π^* makes contributions of the opposite signs. These changes in bond order are, of course, consistent with the usual resonance-theory description

FIG. 2. *Potential energy as a function θ_{a1} for ground and excited states of* (*a*) *unhindered,* (*b*) *slightly hindered, and* (*c*) *moderately hindered stilbenes.*

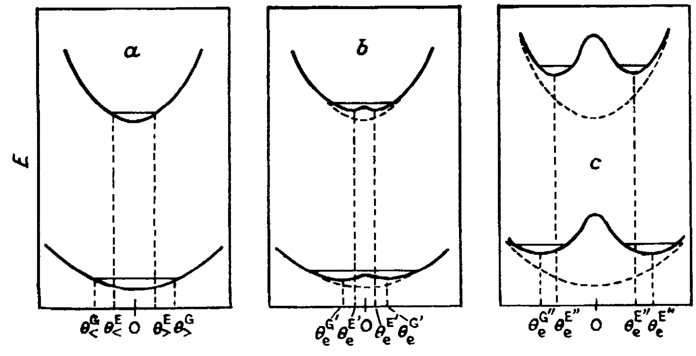


FIG. 3. *Potential energy as a function $\theta_{aa'}$ for ground and excited states of* (*a*) *unhindered,* (*b*) *slightly hindered, and* (*c*) *moderately hindered stilbenes.*

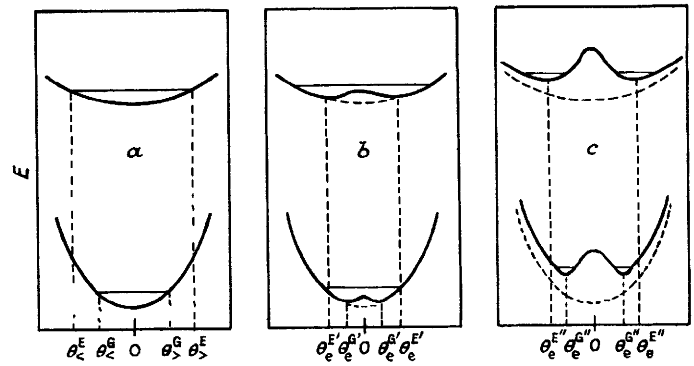
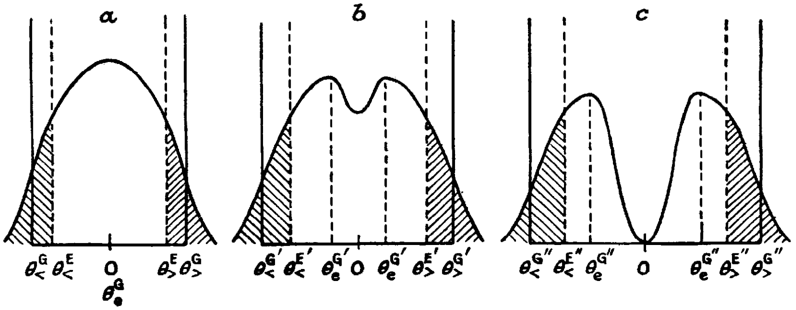


FIG. 4. *Schematic representation of the probability of a transition allowed by the Franck–Condon principle as a function of θ_{a1}.*



of the two states, in which excitation in the $N \longrightarrow V$ transition is ascribed to a decrease of the importance of state (I) and an increase in the importance of state (II).

These considerations then lead to the potential-energy diagrams given in Figs. 2(*a*) and 3(*a*). Examination of these Figures indicates that the vibrational twist about the a–1 bond reduces the intensity below that predicted from the oscillator strength owing to the application of the Franck–Condon principle. This is readily apparent in Fig. 4(*a*) which shows the distribution function as a function of θ_{a1}. Classically, the ground state in its lowest vibrational level may be found between $\theta^{G}_{<}$ and $\theta^{G}_{>}$ indicated as solid vertical lines in Fig. 4(a), and the excited state between $\theta^{E}_{<}$ and $\theta^{E}_{>}$, indicated as broken vertical lines. According to quantum mechanics, of course, these values are not rigid limits, but may be exceeded, though with drastically reduced probability. The shaded areas then correspond approximately to the conformations from which excitation is forbidden, and the theoretical oscillator strength should be multiplied by the ratio of these areas to the total area under the curve. A similar limitation does not exist with respect to the *a–a′* bond, since the excited-state curve is shallower than that for the ground state.

In considering slightly hindered molecules, it appears obvious that, upon twist by just a few degrees, since the hindering is slight, the potential-energy curves of hindered and unhindered molecule should become identical. Near $\theta = 0°$, however, a steric repulsion energy (E_S) raises the curves for the hindered molecule above those for the unhindered one. The minima probably no longer occur at $\theta = 0°$; instead, there should be a very flat and slight maximum there, and shallow minima a few degrees displaced from 0°. It appears possible, or even likely, that even the zero-point vibrational level lies above the central minimum.

In order to describe quantitative differences between effects on ground and excited states, the following quantities are conveniently defined: the equilibrium value of θ in the ground state is denoted by $\theta_e{}^{G'}$ and in the excited state by $\theta_e{}^{E'}$, where the prime identifies the slightly hindered molecule. The corresponding quantities in the unhindered molecule are $\theta_e{}^{G}$ and $\theta_e{}^{E}$ (both, of course, are zero). Energy differences also are required, and the energy at the potential minimum in the ground and the excited state, respectively, of the unhindered molecule are denoted by E^{G} and E^{E}, in the hindered one as $E^{G'}$ and $E^{E'}$.

Thus far the considerations apply equally to $\theta_{aa'}$ and to θ_{a1}. In estimating differences between the quantities just defined, however, the two angles must be treated separately. For θ_{a1}, the bond order increases on excitation and the resulting greater resistance to twist leads to $\theta_e{}^{G'} > \theta_e{}^{E'}$. However, since $\cos\theta$ is a very slowly changing function of θ near $\theta = 0°$, and since the steric repulsion energy also is quite small, $E^{G'} - E^{G} \approx E^{E'} - E^{E}$ [Fig. 2(*b*)]. The excitation energy of the slightly hindered molecule is then essentially the same as in the unhindered molecule; no hypsochromic effect should be noted. Construction of the distribution analogue of Fig. 4(*a*) shows, however, that angles $\theta^{E'}_{>}$ and $\theta^{E'}_{<}$ for the hindered molecule do not exceed the corresponding values for the unhindered one nearly as much as $\theta^{G'}_{<}$ and $\theta^{G'}_{>}$ of the hindered molecule exceed $\theta^{G}_{<}$ and $\theta^{G}_{>}$ of the unhindered one. The result, then, is Fig. 4(*b*) where the ratio of the shaded area—which again corresponds to the population of conformations from which excitation is forbidden—to the total area under the curve is seen to be larger than in Fig. 4(*a*). Consequently, the hypochromic effect in slightly hindered molecules may be explained as a Franck–Condon effect resulting from the twist of angle θ_{a1}. It will be seen in what follows that no alternative explanation appears reasonable for the slightly hindered case.

Consideration of $\theta_{aa'}$ is quite analogous: $p_{aa'}{}^{E} < p_{aa'}{}^{G}$ leads to $\theta_e{}^{G'} < \theta_e{}^{E'}$; again $E^{G'} - E^{G} \sim E^{E'} - E^{E}$ is very probable. The result is the potential-energy curve in Fig. 3(*b*), which shows that no Franck–Condon effects are to be expected.

In the case of moderate steric hindrance the situation is somewhat more complicated. The potential-energy curves must have a fairly high and reasonably steep maximum at $\theta_{aa'} = 0°$ and $\theta_{a1} = 0°$. The equilibrium values $\theta_e{}^{G''}$ (double primes identify the moderately hindered molecule) for both $\theta_{aa'}$ and θ_{a1} occur at considerably larger values of θ than in the slightly hindered case. The potential energy curves will asymptotically approach those of the unhindered case, but only at relatively large values of θ—unless the hindering groups are so bulky that even the completely twisted states are hindered, in which case the chromophores are isolated. The steric repulsion energies $E_s{}^{G''}$ and $E_s{}^{E''}$, *i.e.*, at $\theta = 0°$ the height of the maximum above the unhindered minimum, should also be considered.

For the *a*–1 twist $\theta_e{}^{G''} > \theta_e{}^{E''}$, and $\theta_e{}^{G''} \gg \theta_e{}^{G'}$. But in this case the distortion in θ is large. Since $\cos \theta < 1$, and because of $p_{a1}{}^{G} < p_{a1}{}^{E}$, $E^{G''} - E^{G} < E^{E''} - E^{E}$. Further, contraction of the *a*–1 bond upon excitation will increase $E_s{}^{E}$ slightly over $E_s{}^{G}$; this difference, however, is probably small enough to be negligible, since the small increase in p_{a1} should lead to a contraction of no more than 0·01—0·02 Å. With these considerations as basis, the potential-energy diagram given in Fig. 2(*c*) is drawn. The excited-state energy is raised more than the ground-state energy by the twisting; *i.e.*, the larger difference $E^{E''} - E^{E}$ than $E^{G''} - E^{G}$ leads to the observed hypsochromic shift without intervention of the Franck–Condon principle. Similarly, calculation of the transition moment by crude semi-empirical LCAO MO theory leads to a reduced value in the moderately twisted case and is capable of explaining the hypochromic effect. However, construction of the distribution function [Fig. 4(*c*)] corresponding to the potential energy diagram of Fig. 2(*c*) also shows a Franck–Condon hypochromic effect similar to that one discussed for slightly hindered molecules.

In considering the *a*–*a*′ twist situation, $\theta_e{}^{G''} < \theta_e{}^{E''}$ owing to the decrease in bond-order $p_{aa'}$ on excitation, and for the same reason $E^{G''} - E^{G} < E^{E''} - E^{E}$. Owing to the lengthening of the *a*–*a*′ bond upon excitation, the maximum at $\theta_{aa'} = 0°$ is higher in the ground than in the excited state, *i.e.*, $E_s{}^{G} > E_s{}^{E}$; the difference also should be small, though larger than for the *a*–1 bond owing to the greater change in $p_{aa'}$. These considerations lead to the construction of the potential-energy diagram of Fig. 3(*c*). It is readily seen that the Franck–Condon principle produces no limitations on wavelengths and intensity. The total-energy change between the ground and the excited state does not readily appear from these diagrams, and will be discussed below after consideration of the stretching modes.

The Stretching Modes.—The potential-energy curves as a function of the distances may be expected to have the shape of Morse curves. For the ground states, the known equilibrium distance locates the minimum, and the shape of the curve can be approximated from the force constants. The minima for the excited state may be estimated from the change in double-bond character on excitation; this is readily estimated from rough LCAO molecular-orbital calculations (cf. Table 2, giving the results of these calculations). It is thus found that excitation of one electron from the highest occupied (π) to the lowest unoccupied (π^*) orbital decreases the bond order $p_{aa'}$ from 2·00 to 1·68, and simultaneously increases the bond order p_{a1} from 1·24 to 1·48.† If we assume 1·48 Å as the normal single-bond distance,[6] and 1·34 Å as the normal double-bond distance of two sp^2 carbon atoms, it can be estimated that upon excitation the *a*–*a*′ bond is stretched by approximately 0·05 Å, and the *a*–1 bond compressed by approximately 0·03 Å. Since force constants

TABLE 2.

	Planar stilbene	Hindered stilbene	Isolated chromophores [q]		Planar stilbene	Hindered stilbene	Isolated chromophores
β_{a1} [m]	0·6	0·5	0	$\mathscr{E}$ [n,m]	18·694	18·412	18·400
$\beta_{aa'}$ [m]	1·2	1·1	1·2	$\Delta\nu$ [o.m]	1·508	1·537	2·000
ε [m] of $\psi_8{}^*$...	−0·754	−0·768	−1·000	RE [p,m,q] ...	0·294	0·012	0
ψ_7 ...	0·754	0·768	1·000	T.M.[r]	0·899	0·842	—
$\psi_{6,5}$	1·000	1·000	1·000	$p_{a1}{}^{G}$ [s]	1·244	1·212	1·000
ψ_4 ...	1·054	1·039	1·000	$p_{a1}{}^{E}$	1·48	1·462	1·000
ψ_3 ...	1·436	1·335	1·200	$p_{aa'}{}^{G}$	2·000	2·000	2·000
ψ_2 ...	2·020	2·012	2·000	$p_{aa'}{}^{E}$	1·680	1·640	1·000
ψ_1 ...	2·083	2·050	2·000				

[m] In units of β_{CC} in the ring. [n] The total π-electron energy. [o] The energy of the $N \longrightarrow V$ transition. [p] The resonance energy. [q] Referred to two benzene rings and an ethylene molecule. [r] The transition moment, in arbitrary units. [s] The bond order: the superscript G refers to the ground state, E to the excited state; the subscript identifies the bond.

---

† Jacobs and Coulson [9] give somewhat different bond orders. The above bond orders are based on assumed resonance integrals $\beta_{aa'} = 1·2$, $\beta_{a1} = 0·6$. The value of 2·00 calculated for the *aa*′-bond in the ground state is in agreement with the bond length of 1·33 Å which is substantially the length of a pure double bond.

[9] Jacobs and Coulson, *J.*, 1949, 1983.

also are roughly proportional to bond orders, the same information permits estimation of the shapes of the excited-state Morse curves. Since the subsequent arguments are independent of the quantitative results for these curves, only schematic representations are given in Figs. 5(*a*) and 6(*a*).

Estimation of the corresponding quantities for the hindered molecule is difficult, but the qualitative changes are nevertheless apparent and sufficient for the discussion. Stretching of the *a*–*a*′ bond is favoured by a gain in σ-bond energy, and opposed by a relatively high bond order of the bond; it is ineffective in reducing repulsion between *ortho*-substituents (or hydrogen) and the *a*-hydrogen atom, and hence is not involved in cases of slight hindering. The potential-energy minima of slightly hindered and unhindered molecules, accordingly, should occur at about the same value of r_{aa}, and the corresponding potential-energy curves should practically coincide.

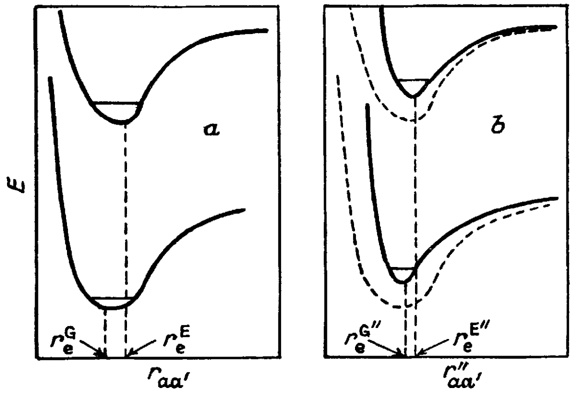


Fig. 5. *Potential energy as a function of $r_{aa'}$ of (a) unhindered and (b) moderately hindered stilbenes.*

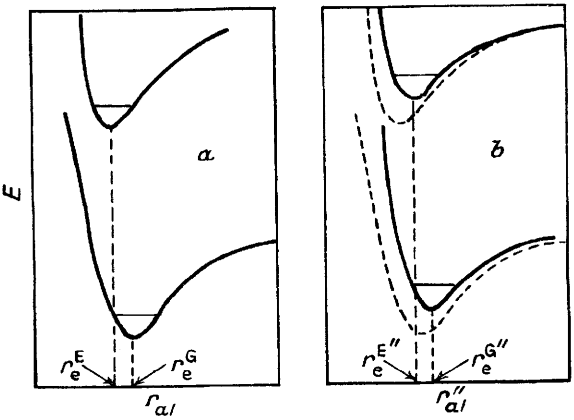


Fig. 6. *Potential energy as a function of r_{a1} of (a) unhindered and (b) moderately hindered stilbenes.*

For the moderately hindered case, the ground-state minimum should occur at somewhat greater distance. At the same time, the potential-energy curves for both hindered and unhindered molecules should approach asymptotically at large $r_{aa'}$, should deviate progressively at low r_{aa} , with the hindered curve always above the unhindered one, and, at $r_{aa'}$ less than the equilibrium value, should rise more sharply because of the high power with which the van der Waals forces responsible for steric effects depend on r. The equilibrium value of r in the ground state is denoted as r_e^G and that in the excited state as r_e^E, both for the unhindered molecule, and the corresponding quantities of the hindered molecule as $r_e^{G''}$ and $r_e^{E''}$. The energy values at the potential minimum in the ground and the excited state respectively are denoted by E^G and E^E of the unhindered molecule, and by $E^{G''}$ and $E^{E''}$ for the corresponding quantities for the hindered molecule. The relative magnitudes of the quantities $E^{G''} - E^{G}$, and $E^{E''} - E^{E}$ are of importance as are the quantities $r_e^{G''} - r_e^{G}$ and $r_e^{E''} - r_e^{E}$. Since the excited state is stretched, relative to the ground state, it appears that the steric repulsion energy, $E^{E''} - E^{E}$, should be less in the excited state than the corresponding quantity, $E^{G''} - E^{G}$, in the ground state: $E^{E''} - E^{E} < E^{G''} - E^{G}$. Similarly, it is expected that $r_e^{E''} - r_e^{E} < r_e^{G''} - r_e^{G}$. The resulting potential-energy diagram is given in Fig. 5(*b*). The result of these inequalities is that any change of the effects due to the Franck–Condon principle would result in a bathochromic shift and a hyperchromic effect for the hindered molecule, in contradiction to the experimental facts. Accordingly, it may be concluded that any Franck–Condon effects due to changes in $r_{aa'}$ are either negligible or subsidiary to other effects.

The *a*–1 bond may also be somewhat effective in relieving steric strain, although probably less so than the *a*–*a'* bond. Hence the direction of the shifts in the minima, and the qualitative changes should be the same for these bonds. However, since the *a*–1 bond is compressed by excitation, the inequality of the changes of r_e is reversed, leading to $r_e^{E''} - r_e^{E} > r_e^{G''} - r_e^{G}$. Since the change in bond length is quite small, $r_e^{E} - r_e^{G}$ is quite small, indicating that application of the Franck–Condon principle should not reduce the intensity of the unhindered molecule appreciably, Fig. 6(*a*). This small reduction would be further reduced in the hindered molecule, Fig. 6(*b*), and again the Franck–Condon principle, if involved at all, leads to predictions contrary to experimental fact. Accordingly changes in bond lengths of any of the bonds cannot account for the spectral changes produced by the hindered molecule.

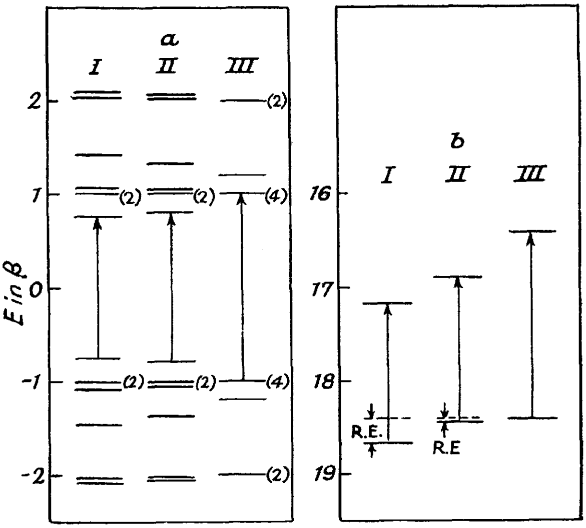


FIG. 7. (*a*) *One-electron energy and* (*b*) *the term-level diagrams. The numbers in parentheses in* (*a*) *indicate degeneracy. I, Unhindered stilbenes; II, hindered stilbenes; III, isolated chromophores.*

π-Electron Energies.—Having considered the various deformations effective in reducing steric strain and their potential-energy diagrams, and having found that the Franck–Condon principle correctly predicts the hypochromic effect in slightly hindered and at least a part thereof in moderately hindered molecules, but fails to provide an explanation for the hypsochromic effect in the latter, we can now examine the total-energy level and geometry difference due to excitation. Since the *a*–1 bond is both twisted and stretched in hindered molecules, the resonance integral β''_{a1} in the moderately hindered molecule should be appreciably reduced from the value β_{a1} in the unhindered molecule. The deformations relieving steric strain, in order of importance, are (*a*) *a*–1 twist, (*b*) *a*–*a'* twist, (*c*) *a*–*a'* stretch, (*d*) *a*–1 stretch, aside from the spectroscopically uninteresting modes listed under (*e*) and (*f*) above. Twists (*a*) and (*b*) result in reduction of β_{a1} to $\beta''_{a1} = \beta_{a1} \cos \theta_{a1}$, and $\beta_{aa'}$ to $\beta''_{aa} = \beta_{aa'} \cos \theta_{aa'}$, respectively. Since β's monotonically decrease from a maximum value at zero internuclear distance to a zero value at infinite distance, stretches (*c*) and (*d*) lead to additional, though smaller, decreases in the respective β's. As a result, hindrance should cause a larger relative reduction in β_{a1} than in $\beta_{aa'}$. These considerations are made the basis of crude semi-empirical LCAO MO calculations. The results given in Table 2 show that the reduction in the β's alone correctly predicts the trends of the experimental observations in the moderately hindered case. It should be noted that these calculations do not take account of changes in geometry on excitation, so that the total π-electron energy differences are approximated as the energy differences between the levels of the excited electron before and after excitation, and any simultaneous change of the energies of any other electrons, due to a change in geometry and a consequent change in resonance integrals, are neglected. This neglect appears justified since differences in geometry between ground and excited state are probably much smaller than the changes due to steric distortion. Fig. 7(*a*) shows the energy level diagram based on the calculations and addition of the energy values correctly indicates the decrease in stability in the hindered forms, and at the same time the spreading of the highest occupied and lowest unoccupied levels responsible for the hypsochromic shift. The data are summarized in Fig. 7(*b*), where total π-electron energies of ground and the excited states are given.

In both parts of Fig. 7 the column at the far right represents the completely hindered case, in which the chromophores are isolated. In this case it is assumed that the *a*–*a'* bond remained untwisted for the sake of later generalization, although this probably would not be the case.

Crude calculations of oscillator strength (transition moments) were also made by LCAO theory. The calculations for the moderately hindered case ($\beta_{a1} = 0{\cdot}5$, $\beta_{aa'} = 1{\cdot}1$) correctly show the observed hypochromic effect. The oscillator strength appears to be relatively insensitive to cos θ, and hence, if $1 - \cos\theta$ can be neglected as far as energy calculations are concerned, it can probably also be neglected when dealing with intensity calculations. Calculations of oscillator strength based on a change in β are thus incapable of explaining a hypochromic without accompanying hypsochromic effect, and the Franck–Condon effect due to changes in θ_{a1} on excitation must be called upon to explain this situation. In the case of moderate hindrance, where both hypochromic and hypsochromic effects are present, it is difficult to decide whether the hypochromic effect should be assigned to a reduction in oscillator strength or to a Franck–Condon effect, or to make an assignment of the relative contribution of each of these. In the special case of *cis*-stilbene, as additional factor contributing to the hypochromic effect is the shorter distance between the ends of the chromophore. A similar situation in the acetylcyclohexenes has been discussed by Turner and Voitle.[1]

GENERALIZATION

It now remains to attempt to generalize the treatment, by extension to other molecules or, better, to various general types of molecule. The most important general case is probably that in which the steric strain is most efficiently and best relieved by twisting about—and possibly stretching of—an " essential " single bond (one which is a single bond in the most important resonance structures; an essential double bond is one which is double in them).

In most known cases such a bond attains more double-bond character in the excited state, corresponding to a transition predominantly represented by R–R' in the ground state, and by $\pm$R=R$\mp$ in the excited state.† The *a*–1 bond of stilbene is such a bond, and

---

† A somewhat different case, 1-acetylazulene, is discussed by Heilbronner and Gerdil (*Helv. Chim. Acta*, 1956, **39**, 1996) in which the bond order of the essential single bond about which twist relieves steric strain, *decreases* on excitation. The applicable potential energy diagram would correspond more to Fig. 3 than to Fig. 2, leading to no Franck–Condon effect, but the energy-level scheme would correctly predict the observed bathochromic shift, as pointed out by Heilbronner and Gerdil. These authors consider other molecules and come to substantially the same conclusions to those reached here in the π-electron calculations.

the most commonly investigated steric effects in absorption spectra are of this type; examples are acetophenones[10] and related compounds,[11] anilines,[12] acetanilides,[13] biphenyls,[14] binaphthyls,[15] etc. In such cases, Figs. 2(*a*), (*b*), and (*c*) are representative potential energy diagrams for R–R′ twist, and Figs. 6(*a*) and (*b*) for R–R′ stretch respectively, and Figs. 4(*a*), (*b*), and (*c*) give the frequency distribution as a function of angle of twist. From these diagrams it can be predicted that such steric hindrance must lead to a Franck–Condon hypochromic effect. Examination of Fig. 7(*a*) also indicates that moderate hindrance (*i.e.*, hindrance that produces a *significant* reduction in the β for the essential single bond) produces a hypsochromic effect, since the highest occupied level in the unhindered molecule must lie above the highest occupied level in the pure chromophores, and reduction of the β's produces a monotonic progression of the energy of this level from the one to the other. A similar progression of the lowest unoccupied level from its position for the unhindered molecule below its value for the separated chromophore to the latter also further contributes to this hypsochromic effect. Similar monotonic shifts of energy levels from the unhindered to the completely hindered molecule also permit a prediction of the effect of hindrance of other than the longest wavelength ($N \longrightarrow V$) transition, provided that such transitions can be identified with specific one-electron transitions. It appears very likely that the red shifts observed by Klevens and Platt for hindered anilines[12] occur in transitions which correspond to some of the higher transitions in Fig. 7, for which also blue shifts would be expected (*e.g.*, $\psi_4 \longrightarrow \psi_{11}$, or $\psi_3 \longrightarrow \psi_8$).

Another important case is that in which, upon excitation, the bond order of an essential double bond decreases, *i.e.*, a transition in which a ground state R=R′ is excited to $\pm$R–R′$\mp$. A case of this type would be represented by hindered ethylenes. Other cases of this type are unlikely to be found readily, since generally twisting about essential single bonds adjacent to the essential double bond will be more effective in relieving strain; however, it is conceivable that such systems might be produced by imposing other steric requirements. The case of the ethylenes is slightly different from those of more complicated molecules. The planarity of the ground state of ethylene is due to the bonding nature of the molecular orbital containing the two π-electrons. Excitation of one of them to an antibonding orbital results in a slight destabilization, compared with two isolated carbon atoms, and in the stable configuration of ethylene the two CH_2 groups are perpendicular to each other. In the case of sterically hindered ethylenes, the Franck–Condon principle leads to a *batho*chromic shift and a *hyper*chromic effect. If the essential double bond is, however, part of a conjugated system, the planarity of the molecule is insured by the co-operative effect of all the π-electrons, and excitation of one of them to an antibonding orbital is insufficient to destroy the planarity. In such a case the potential energy diagram for R–R′ twist and stretch would be given, respectively, by Figs. 3(*a*), (*b*), and (*c*) and Figs. 5(*a*) and (*b*) for the unhindered and the hindered molecules. On the basis of these diagrams one would predict much smaller effects; a very small hypochromic effect due to the twist and a very small hyperchromic one due to the stretch, for slightly hindered molecules, would largely cancel. For more strongly hindered molecules, also, the intensity should not be greatly affected, but a bathochromic shift should result from the twist [Figs. 3(*c*) and 7(*b*)].

This work was supported in part by the Office of Ordnance Research of the U.S. Army.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI,
CINCINNATI 21, OHIO, U.S.A.

[*Received, September 14th*, 1959.]

---

[10] Braude and Sondheimer, *J.*, 1955, 3754.
[11] Hedden and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 3744.
[12] Klevens and Platt, *ibid.*, 1949, **71**, 1714.
[13] Burgers, Hoefnagel, Verkade, Visser, and Wepster, *Rec. Trav. chim.*, 1958, **77**, 491; Ungnade, *J. Amer. Chem. Soc.*, 1954, **76**, 5133.
[14] Pickett, Walter, and France, *J. Amer. Chem. Soc.*, 1936, **58**, 2296.
[15] Friedel, Orchin, and Reggel, *ibid.*, 1948, **70**, 199.