Relations between the Electronic Absorption Spectra and the Spatial Configurations of Conjugated Systems. XII. The Intensity and the Shape of the Conjugation Band

By Hiroshi SUZUKI

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The preceding parts[1] of this series dealt mainly with a rather restricted aspect of the theme. That is, they dealt mainly with the relation between the wavelength position of the absorption maximum of the conjugation band and the most probable configuration of the molecule in some conjugated hydrocarbon systems, such as biphenyl, styrene and stilbene. In the present paper, other aspects of the subject, especially the relations between the intensity, as well as the shape of the conjugation band, and the spatial configuration of the molecule, are discussed for the foregoing systems as representatives of alternant hydrocarbon systems.

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[1] H. Suzuki, This Bulletin, (I) 32, 1340; (II) 1350; (III) 1357 (1959); (IV) 33, 109; (V) 379; (VI) 389; (VII) 396; (VIII) 406; (IX) 410; (X) 613; (XI) 619 (1960).

Calculation of the Transition Moment as a Function of the Angle of Twist

It is well known that in such conjugated hydrocarbon system as the foregoing, steric hindrance to the planarity of the system exerts a hypochromic as well as a hypsochromic effect on the conjugation band.

The steric hindrance may be considered to be relieved, to a first approximation, only by a twist of the formally single bond or bonds, e.g., the co-annular bond in the biphenyl system, the bond linking the phenyl group to the ethylenic carbon atom in the styrene system, and the similar bonds in the stilbene system. (These " single " bonds are referred to as the pivot bonds.) On the basis of this assumption, in the preceding parts of this series, the energy of a one-electron transition from the highest occupied π-orbital, ψ_{+1}, to the lowest vacant one, ψ_{-1}, was calculated, by the simple LCAO MO method, as a function of the angle of the twist of the pivot bond for each of these systems and was correlated with the wavelength of the maximum of the conjugation band for a number of the compounds of the system. In spite of the simplicity of the method used, the correlation was almost completely satisfactory. Thus, it may be said that an almost satisfactory explanation of the steric hypsochromic effect in these conjugated systems was obtained. Therefore, it may be of some interest to see whether the steric hypochromic effect, i.e., the reduction of the intensity of the band due to steric hindrance to the planarity of the conjugated system, can be explained by extending the simple MO treatment.

The resonance integral of the atomic orbitals χ_i and χ_j is denoted by $\rho_{ij}\beta$, β representing the π-π resonance integral for adjacent carbon atoms in the benzene ring. The parameter, ρ_{ij}, is determined by the distance, R_{ij}, between atoms i and j as well as by the angle of twist, θ_{ij}, of the bond, i.e., the angle by which the axes of χ_i and χ_j are twisted with respect to each other. If it is assumed that the bond length, R_{ij}, is constant, ρ_{ij} can be taken to be proportional to cos θ_{ij}.

On the basis of the orbital energies calculated as functions of ρ_{piv} in the preceding parts of this series, the coefficients of the atomic orbitals in the molecular orbitals ψ_{-1} and ψ_{+1} and then the transition moment, $M_{-1,+1}$, have been calculated as functions of ρ_{piv}. The transition moment is, needless to say, expressed as:

$$M_{-1,+1}=\sqrt{2}\int\psi_{-1}q\psi_{+1}\mathrm{d}\tau$$

where q and $\mathrm{d}\tau$ are the position coordinate of the electron and the volume element of the space of the coordinate respectively. By the way, the subscript $-1,+1$ refers to quantities concerning the transition from ψ_{+1} to ψ_{-1}, while the subscript piv refers to quantities concerning the pivot bond. These subscripts are subsequently often omitted for the sake of brevity if no confusion is possible. In the calculations, the relation between ρ and θ as well as R assumed in the preceding parts has been used for each system, and all the bond angles at the carbon atoms in the conjugated skeleton have been assumed to be 120°. The results are shown in Fig. 1, in which the values of the square of the transition moment, namely, the dipole strength of the transition (in units of Å²), are plotted against θ_{piv}.

The oscillator strength, f, is related to the transition moment by the usual equation;

$$f=1.085\times10^{-5}\nu M^2$$

where ν is the wave number (in cm^{-1}) at which the absorption due to the transition occurs. In the previous papers, the wave number to be observed was correlated with the transition energy, ΔE, calculated as a function of θ for each of the systems. Accordingly, by the use of the relation, the f-value can be calculated as a function of θ for each system. The calculated f-value, which is designated as f_{theor}, for the stilbene system is also graphed in Fig. 1.

It can be clearly seen in this figure that the dipole strength of the transition, as well as the oscillator strength, of each system becomes

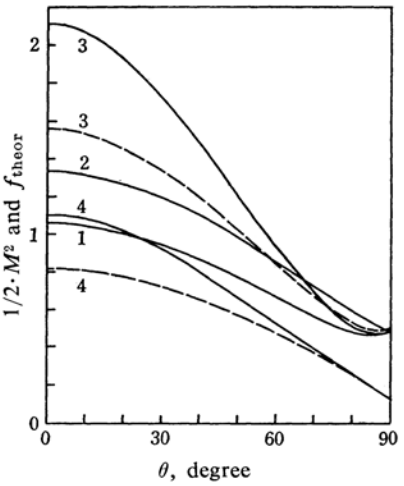

Fig. 1. Relations between the transition moment, M, as well as the calculated oscillator strength, f_{theor}, of the conjugation band and the angle of twist of the "single" bond, θ. Solid lines are for $1/2\cdot M^2$ (in Å²); broken lines, for f_{theor} 1, styrene 2, biphenyl 3, *trans*-stilbene 4, *cis*-stilbene.

smaller as the value of θ becomes larger. This means that the intensity of the conjugation band will become lower as the deviation from the planarity of the conjugated system increases, a trend which is in agreement with observation. It may be noted here that the variation in the dipole strength of the transition associated with the variation of ρ_{pIV} is roughly linear in each of the systems.

A Comparison of the Theoretical Values with the Experimental Values of Oscillator Strength

The oscillator strength can be estimated from the absorption curve by means of the usual equation:

$$f=4.317\times10^{-9}\int\varepsilon_{\nu}\mathrm{d}\nu$$

where ε_{ν} is the molar extinction coefficient at wave number ν and the integral is the integrated intensity of the absorption band concerned. The value of the oscillator strength estimated from the observed spectrum is designated as f_{exp}.

In Table I, for some compounds of the conjugated systems under consideration and, in addition, for butadiene, the values of f_{theor} and f_{exp} are listed, together with some relevant data.

The f_{theor}-Values.—The values of θ are those evaluated from the wavelengths of the absorption maxima in the previous parts of this series, and the transition moments have been calculated on the basis of these θ values. That is, the transition moment of each compound has been calculated for the most probable configuration of the conjugated system, and no electronic (probably small hyperchromic) effects which the substituents may exert on the absorption intensity have been taken into account.

For tetraphenylethylene, the model in which all of the phenyl groups are rotated out of the plane of the central ethylenic bond to the same extent was used as the basis for the calculation of the transition moment, according to the conclusion made in Part VI of this series.

For butadiene, the calculation has been carried out on the basis of the planar s-trans model in which the lengths of the "double" bonds and of the "single" bond are 1.34Å and 1.48Å respectively.

The f_{exp}-Values.—The f_{exp}-values for most compounds were estimated from the absorption spectra reported in Parts I, II, V and VII of this series. The spectra of biphenyl, tetraphenylethylene and tolan reported in Parts I and VI were found to be somewhat inaccurate with respect to the absorption intensity. Accordingly, the f_{exp}-values for these compounds (the entry numbers 4, 13 and 14) were estimated on the basis of the newly redetermined spectra. The experimental data for the entry

TABLE I

No.	Compound	λ mμ	ε $\times10^{-2}$	θ degree	M^2 Å^2	f_{theor}	f_{exp}	$\frac{f_{\mathrm{theor}}}{f_{\mathrm{exp}}}$	$\frac{f_{\mathrm{exp}}}{\varepsilon}$ $\times10^7$	$\Delta\nu$ $\times10^{-1}$ cm^{-1}
1	Butadiene (in *n*-hexane)	217	209	0	2.334	1.167	0.53	2.20	254	—
2	Styrene	248	148	0	2.120	0.927	0.327	2.84	222	—
3	Biphenyl (KCI disk)	253	—	0	2.677	1.148	—	—	—	—
4	Biphenyl	247	167	23	2.503	1.100	0.411	2.68	246	254
5	Biphenyl (vapor, 170°C)	238	121	42	2.159	0.984	0.316	3.11	262	—
6	*o*-Methylbiphenyl	235	100	58	1.772	0.818	0.261	3.13	261	260
7	*trans*-Stilbene	294	280	0	4.221	1.557	0.739	2.11	264	307
8	*trans*-α, α'-Dimethylstilbene	243	123	58	1.951	0.870	0.350	2.49	285	323
9	*trans*-α, α'-Diethylstilbene	237	111	63	1.696	0.778	0.330	2.36	298	335
10	*cis*-Stilbene (in ethanol)	280	105	28	1.882	0.729	0.323	2.26	309	311
11	*cis*-α, α'-Dimethylstilbene	252	89	52	1.276	0.549	0.329	1.67	371	450
12	*cis*-α, α'-Diethylstilbene (in ethanol)	244	77	58	1.110	0.494	0.270	1.83	349	372
13	Tetraphenylethylene	309	142	35	2.566	0.902	0.393	2.30	278	266
14	Tolan	280	316	0	4.804	1.862	0.700	2.66	222	233

The notation is as follows: λ and ε, the wavelength and the molar extinction coefficient of the maximum of the conjugation band respectively; θ, the angle of twist of the "single" bond in the most probable configuration; M, the calculated transition moment; f_{theor} and f_{exp}, the theoretical and the experimental oscillator strength respectively; $\Delta\nu$, the wave number interval between the absorption maximum and the point of half the maximum intensity at a longer wavelength than the maximum.

numbers 1[2,3], 2[4], 3[5] and 5[6] have been taken from papers of other authors. All the spectral data are for the solution in *n*-heptane at room temperature except where otherwise indicated.

It is difficult to determine unambiguously the intrinsic band envelope and, hence, the integrated intensity of the conjugation band as differentiated from neighboring bands. For each of the compounds of entry numbers 4, 7, 10, 13 and 14, the area under the absorption curve at wave numbers lower than the absorption minimum between the conjugation band and the neighboring band lying at higher wave numbers was taken as an approximation of the integrated intensity of the conjugation band, since with these compounds the conjugation band is comparatively well resolved from its neighbor.

With the compounds of entry numbers 6, 8, 9, 11 and 12, the conjugation band itself is situated at quite a high wave number and has quite a low intensity; hence, the resolution of the band from the neighboring band is very unsatisfactory. Therefore, for these compounds, twice the area under the absorption curve at wave numbers lower than the absorption maximum was taken as a rough appoximation of the integrated intensity of the conjugation band.

Comparison of f_{theor}- and f_{exp}-Values.—It is well known that the value of f calculated by the simple MO method is in general too high by a factor of about 2∼3. This general tendency is considered to be due to the essential character of the method, which does not take account of interactions among electrons and hence tends to over-estimate the delocalization of the molecular orbitals[7]. This appears to be inevitable when any one single electronic configuration is used. In this respect, the present calculation is not an exception. Thus, the ratios of f_{theor} to f_{exp} are about 2∼3.

Apart from the discrepancy in the absolute values, quite a good correspondence is found between the f_{theor} values and the f_{exp} values. This can be seen more clearly in Fig. 2, in which the f_{theor} values are plotted against the corresponding f_{exp} values. Considering the uncertainty involved in the estimation of the f_{exp} values, as well as the simplification made in the calculation of the f_{theor} values, it may be said that the correspondence is rather unexpectedly good. Especially, it may be noted that the points for the compounds belonging to the stilbene system (entry numbers 7, 8, 9, 10 and 13), with the exception of two *cis*-dialkylstilbenes and tolan, fall nearly on a smooth line passing through the origin.

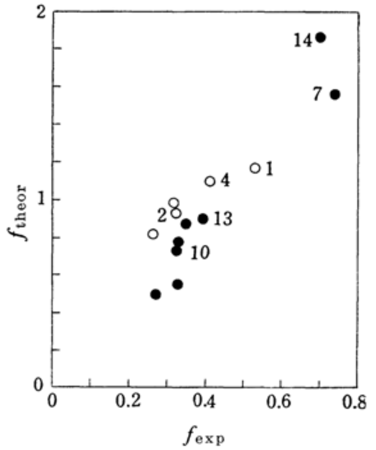

Fig. 2. Relations between the theoretical values, f_{theor}, and the experimental values, f_{exp}, of the oscillator strength of the conjugation band. ○, for the compounds of the entry numbers 1—6 in Table I; ●, for the compounds of the entry numbers 7—14 (the compounds of the stilbene system, including tolan).

This almost satisfactory correspondence of the f_{theor} values to the f_{exp} values may be considered to validate the present treatment. Thus, it may be concluded that the reduction of the intensity, as well as the shift toward shorter wavelengths, of the conjugation band caused by steric hindrance to the planarity of the conjugated system has been almost satisfactorily explained solely by the change in the π-electronic states of the molecule associated with the change of the most probable configuration.

Basic Assumptions in the Present Treatment

One of the basic assumptions underlying the treatment developed throughout the present series of papers is that the steric hindrance to the planarity of the conjugated system is relieved to a first approximation only by a twist of the formally single bond or bonds. Any twist of such a bond should not affect the σ-bond energy, and, since such a bond has a relatively low π-bond order in the electronic ground state, the loss of the delocalization energy of the π-electrons associated with the twist should be relatively small. Furthermore, it is expected that such a twist will, in most cases, rapidly reduce the steric repulsion

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[2] K. B. Alberman, R. N. Haszeldine and F. B. Kipping, *J. Chem. Soc.*, **1952**, 3284.

[3] C. A. Coulson and J. Jacobs, *Proc. Roy. Soc.*, **A206**, 287 (1951).

[4] D. F. Evans, *J. Chem. Phys.*, **23**, 1429 (1955).

[5] J. Dale, *Acta Chem. Scand.*, **11**, 650 (1957).

[6] F. Almasy and H. Laemmel, *Helv. Chim. Acta*, **33**, 2092 (1950).

[7] See, for example, Ref. 3, and also R. S. Mulliken and C. A. Rieke, *Rep. Progr. Phys.*, **8**, 231 (1941).

between non-bonding atoms. The above assumption is quite admissible.

Two other important underlying assumptions are that the molecules with the most probable configuration in the electronic ground state make the most important contribution to the absorption band and that the absorption maximum corresponds to the vertical transition in such molecules. These assumptions might appear to be self-evident. However, since the explanations of the steric hypochromic effect proposed by some other authors seem to be based on an idea quite opposed to this assumption, and, further, in order to provide a basis for a later discussion of the shape of the band, they will be discussed here in some detail.

The potential energy curve of any electronic state for the twist of a "single" bond can be considered to be determined primarily by the sum of the π-electronic energy of the state and of the steric repulsion energy as functions of the angle of twist. Such a potential energy curve may be relatively shallow; hence, the separations of the vibrational levels may be relatively small, compared, for example, with those for the stretching vibrational mode of a "double" bond.

According to the classical theory, the molecules in each vibrational level can be considered to stay predominantly at the turning points of the vibrational motion. Therefore, according to the Franck-Condon principle, the most probable of the electronic transitions which a molecule in a vibrational state associated with the electronic ground state can give rise to should be the transition vertically upward in the potential energy diagram from each of the turning points of the vibrational level to the point on the potential energy curve of the electronic upper state. The energy of such a vertical transition is the difference between the potential energies of the two points and, hence, should be equal to the difference between the π-electronic energies in the configuration characterized by the angle of twist, the contributions of other factors such as steric repulsion energy and σ-electronic energy to the potential energies of the two points being considered to be identical because the transition does not involve any change in the spatial configuration of the molecule. This consideration justifies that treatment in the present series by which the energy difference between the two π-orbitals, ψ_{-1} and ψ_{+1}, calculated as a function of θ, namely, $\Delta E_{-1,+1}(\theta)$, has been correlated directly with the wave number of the observed absorption band.

The wave number corresponding to $\Delta E(\theta)$ is denoted by $\nu(\theta)$, and the transtion moment and the oscillator strength of this transition are denoted by $M(\theta)$ and $f(\theta)$ respectively. The population ratio of the configuration characterized by θ in the electronic ground state is denoted by $P^G(\theta)$. The value of θ at which the value of $P^G(\theta)$ is at its maximum is denoted by $\theta^G{}_{\max}$, which may be considered to agree approximately with the value of θ at the minimum of the potential energy curve, namely, $\theta^G{}_{eq}$, in which the subscript eq is an abbreviation for "equilibrium".

The contribution of any configuration to the absorption is proportional to the product of the population ratio of the configuration and the transition probability in the configuration. Accordingly, the absorption intensity, $\varepsilon(\theta)$, at the wave number, $\nu(\theta)$, can be taken to be approximately proportional to $f(\theta)\cdot P^G(\theta)$.

The value of f, as well as that of M^2, decreases comparatively slowly as the value of θ becomes larger, as is seen in Fig. 1. Roughly speaking, the larger the value of θ, the larger the increase of f as well as of M^2 associated with a decrease of θ. Thus, in the conjugated hydrocarbon systems treated in the present paper, the variation of f as well as of M^2 is approximately linear to cos θ.

On the other hand, the distribution curve of $P^G(\theta)$ versus θ may be relatively steep. Thus, the value of $P^G(\theta)$ may decrease comparatively rapidly as the value of θ is separated in both directions from that of $\theta^G{}_{\max}$. In cases where steric hindrance is involved, the larger the steric hindrance, the larger the value of $\theta^G{}_{\max}$ and, probably, the larger the decrease of $P^G(\theta)$ associated with a decrease of θ from $\theta^G{}_{\max}$.

Therefore, it is quite reasonable to expect that the angle of twist, θ, at which the value of $f(\theta)\cdot P^G(\theta)$ is at its maximum agrees almost completely with $\theta^G{}_{\max}$, i. e., the angle of twist in the most probable configuration. Thus, the maximum of the absorption band may be considered to originate in molecules with the most probable configuration.

The oscillator strength of the band should be expressed as:

$$f=\int f(\theta)\cdot P^G(\theta)\cdot d\theta$$

Judging from the above-mentioned feature or the dependence of $f(\theta)$ as well as of $P^G(\theta)$ on θ, it is evident that f can be well approximated by $f(\theta^G{}_{\max})$.

On Some Other Explanations of the Steric Hypochromic Effect

The Explanation of Jaffé and Orchin.—Jaffé and Orchin[8] recently proposed a "Franck-Condon effect" as an important cause of the

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[8] H. H. Jaffé and M. Orchin, *J. Chem. Soc.*, 1960, 1078.

steric hypochromic effect observed with the conjugation band of such sterically hindered compounds as sterically hindered stilbenes. Their basic theory is that only the vertical transitions to the lowest vibrational level of the electronic upper state should be allowed. Thus, according to them, if the values of θ at the turning points of the lowest vibrational level of the twisting mode of the "single" bond in the electronic excited state are denoted by $\theta^{E}{}_{<}$ and $\theta^{E}{}_{>}$, only the molecules with the value of θ in the range between $\theta^{E}{}_{<}$ and $\theta^{E}{}_{>}$ in the electronic ground state can give rise to a transition to the electronic excited state, and any transition in the molecules with θ outside the range is forbidden. Accordingly, the observed intensity of the band should be reduced below the value predicted from the theoretical oscillator strength by the ratio of the number of the molecules with θ in the range to the whole number of the molecules in the electronic ground state. The greater the steric hindrance, the smaller this ratio will be. This is the gist of Jaffé and Orchin's explanation of the "Franck-Condon effect".

This explanation is in conflict with the basic assumptions of the present treatment. From the considerations given above, it is evident that the explanation by Jaffé and Orchin is invalid. In addition, they seem to confuse the probability density distribution in the lowest vibrational state in the electronic ground state with the distribution of population among various vibrational states in the electronic state; furthermore, it seems not to be clear whether they discuss the intensity of the absorption maximum or the integrated intensity of the entire band.

The Explanation of Braude.—The argument of Jaffé and Orchin is similar to the explanation by Braude of the so-called type 1 steric effect, i. e., the decrease in the intensity of the conjugation band without any appreciable accompanying wavelength displacement of the band observed with sterically hindered compounds, e. g., *o*-substituted acetophenones, as compared with the sterically unhindered parent compound. Braude and his co-workers[9,10] ascribed this decrease in the intensity to the decrease in the population ratio of the planar or near-planar configuration in the electronic ground state. This theory means that, with sterically hindered compounds, the maximum absorption does not originate in the most probable non-planar configuration but in the less probable, energetically unfavorable, planar or near-planar configuration; this is contrary to the basic assumptions of the present treatment. The theory of Braude is evidently based on the concept that the absorptions at nearly identical wavelengths should be due to the transitions in the nearly identical configurations; it also tacitly involves the assumption that the transition in non-planar configurations is impossible or nearly so.

In general, the direction and the magnitude of the change of the transition energy caused by a twist of a bond depend on the sign and the magnitude of the change in the π-bond order of the bond associated with the transition[11,12] and, hence, essentially on the nature of the orbitals between which the transition occurs[13]. In some cases, it is possible that a quite large change of the molecular configuration results in substantially no change or a very small change in the transition energy. Therefore, absorptions at the identical wavelength do not necessarily mean that they originate in the identical configuration.

As is shown above, the transition moment varies continuously with θ in the cases of the conjugated hydrocarbon systems. As will be discussed later in this series, the situation is not so very different in the case of the phenylcarbonyl system, i. e., the acetophenone or benzaldehyde system, which was cited by Braude as representative of the systems exhibiting the so-called type 1 steric effect. The assumption that the transition in non-planar configurations is substantially impossible is untenable. Furthermore, it has been demonstrated experimentally by Waight and Erskine[14] that the maximum absorption should be considered to originate in the transition in the most probable non-planar configuration, even in the case of sterically hindered acetophenones.

The Shape of the Conjugation Band

Potential Energy Curves for the Twisting Mode.—It is a notable fact that the conjugation band of *trans*-stilbene exhibits a well-resolved vibrational fine structure, even at room temperature, whereas the bands of sterically-hindered related compounds are structureless. A similar situation can be found in many other conjugated systems.

We shall now attempt, on the basis of the considerations so far described, to relate the shape of the conjugation band to the steric hindrance to the planarity of the conjugation system. With this end in view, the potential

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[9] E. A. Braude and F. Sondheimer, ibid., **1955**, 3754.

[10] W. F. Forbes, "Steric Effects in Conjugated Systems", Ed. by G. W. Gray, Butterworths Scientific Publications, London (1958), p. 62 ff.

[11] E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

[12] R. I. T. Cromartie and J. N. Murrell, *J. Chem. Soc.*, **1961**, 2063.

[13] J. N. Murrell, ibid., **1956**, 3779.

[14] E. S. Waight and R. L. Erskine, Ref. 10, p. 73 ff.

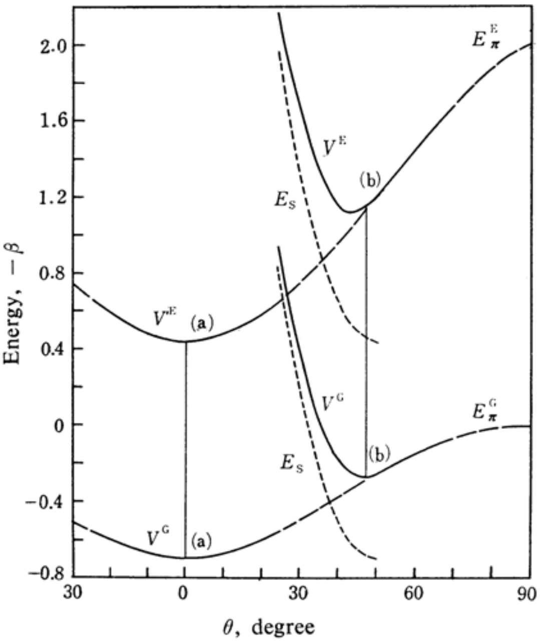

Fig. 3. Potential energy diagram for the stilbene system. V, potential energies (solid lines) as functions of the angle of twist of the "single" bonds, θ: (a) for the sterically unhindered compound; (b) for a sterically hindered compound. E_{π}, π-electronic energies (broken lines). E_{s}, steric repulsion energy (dotted lines).

energy curves for the twisting of the pivot bonds are first examined.

In Fig. 3, the calculated π-electronic energy ($E^{\mathrm{G}}{}_{\pi}$) of the ground state of the stilbene system and that ($E^{\mathrm{E}}{}_{\pi}$) of the excited state which arises from the transition of an electron from ψ_{+1} to ψ_{-1} are plotted against θ, these curves being shown as broken lines. In this figure, the energy of the ground state when θ is 90° is taken as the reference zero energy, while the unit of energy is $-\beta$. By the way, the superscripts G and E refer to the electronic ground state and the electronic excited state respectively throughout the present paper. The quantity $-E^{\mathrm{G}}{}_{\pi}$ is the so-called extra-resonance energy and is approximately proportional to $\rho^2{}_{\mathrm{piv}}$ and, hence, to $\cos^2\theta_{\mathrm{piv}}$. The difference between $E^{\mathrm{E}}{}_{\pi}$ and $E^{\mathrm{G}}{}_{\pi}$ is the transition energy and increases, roughly speaking, linearly with the decreasing value of ρ_{piv} and, hence, of $\cos\theta_{\mathrm{piv}}$. The $E^{\mathrm{E}}{}_{\pi}$-curve is, of course, steeper than the $E^{\mathrm{G}}{}_{\pi}$-curve.

Also in Fig. 3, the curves for the steric repulsion energy (E_{s}) as a function of θ for a hindered case are arbitrarily depicted as dotted lines. The curves for the resultant potential energy (V) as the sum of E_{π} and E_{s} for the unhindered case and for the hindered case are shown as solid lines.

In the unhindered case, the V-curves coincide with the E_{π}-curves; therefore, $\theta^{\mathrm{G}}{}_{\mathrm{eq}}=\theta^{\mathrm{E}}{}_{\mathrm{eq}}=0°$, where θ_{eq} represents the equilibrium angle of the twist, i.e., θ at the minimum of the V-curve.

In the hindered case, the V of each electronic state is regarded as the sum of E_{π} of the state and E_{s}, which is considered to be identical in both the states. Since $E^{\mathrm{E}}{}_{\pi}$ increases more rapidly than $E^{\mathrm{G}}{}_{\pi}$ does as θ becomes larger, there must be this relation: $\theta^{\mathrm{G}}{}_{\mathrm{eq}}>\theta^{\mathrm{E}}{}_{\mathrm{eq}}>0°$.

The E_{s}-curve may be quite steep. The E_{π}-curves are steeper at a larger value of θ, except when θ is extremely large. Therefore, if the steric hindrance is not so slight, the V-curves in the sterically hindered case may be steeper than the corresponding ones in the unhindered case. At least, there seems to be no reason to believe that the latter should be distinctly steeper than the former.

Distribution of Configurations in the Ground State.—As has been mentioned above, the V^{G}-curve in the sterically hindered case may be steeper than that in the unhindered case. Accordingly, the distribution curve of the population of configurations characterized by θ in the electronic ground state, namely, the $P^{\mathrm{G}}(\theta)\sim\theta$ curve, which can be considered to have its maximum at $\theta^{\mathrm{G}}{}_{\mathrm{eq}}$, may be broader in the unhindered case than in the hindered case.

However, if $P^{\mathrm{G}}(\theta)$ is plotted against $\Delta E(\theta)$ or $\nu(\theta)$ instead of θ, a distribution curve with quite different features will result. As has been mentioned already, the configuration characterized by θ can be considered to be characterized also by $\Delta E(\theta)$ or $\nu(\theta)$. $\Delta E(\theta)$ and $\nu(\theta)$ vary roughly linearly with ρ and, hence, with $\cos\theta$. Therefore, if $\theta^{\mathrm{G}}{}_{\mathrm{eq}}$ is small, even though the distribution curve with respect to θ is comparatively broad, the distribution curve with respect to $\Delta E(\theta)$ or $\nu(\theta)$ will be quite steep. This means that, in this case, even quite a wide variation of θ will give rise to the transition in quite a narrow range of wave numbers. On the other hand, if $\theta^{\mathrm{G}}{}_{\mathrm{eq}}$ is fairly large, even if θ varies within a comparatively limited range around $\theta^{\mathrm{G}}{}_{\mathrm{eq}}$, the variation of θ will give rise to the transition in a comparatively wide range of wave numbers. Thus, from the consideration of the distribution of configurations in the electronic ground state, it may be expected that the conjugation bands of the sterically hindered compounds are broader than that of the unhindered parent compound.

By the way, since $-E^{\mathrm{G}}{}_{\pi}$, i.e., the extra-resonance energy, can be considered to be approximately proportional to $\cos^2\theta$, it can be roughly related with $\Delta E(\theta)$ and $\nu(\theta)$ as follows:

$$-E^G_\pi(\theta) \propto [\varDelta E(90^\circ) - \varDelta E(\theta)]^2$$
$$\propto [\nu(90^\circ) - \nu(\theta)]^2$$

Intensity Distribution among Transitions of Vibrational Progression.—The total probability of the transition from a vibrational state associated with the electronic ground state to the electronic excited state is distributed among transitions to vibrational states associated with the electronic excited state in proportion to the square of the overlap integral of the eigenfunctions of the two vibrational states involved.

The vibrational quantum number is represented by v and, as has been mentioned already, the electronic states are denoted by the superscripts G and E respectively. The lowest vibrational state associated with the electronic ground state, i. e., the state for which v^G is 0, is admittedly most densely populated, and the transition from this state should make the most important contribution to the absorption band, as has been discussed above.

In general, for $v=0$, there is a broad maximum of the probability density distribution approximately above the minimum of the potential energy curve. On the other hand, for $v \neq 0$, there is a broad maximum of the probability density distribution in the neighborhood of each of the classical turning points of the vibrational motion, but lying somewhat more toward the center. In a series of transitions from the state for which $v^G=0$, the overlap integral has a maximum value for the transition to the v^E state which has the broad maximum of its probability distribution vertically above the minimum of the potential energy curve of the electronic ground state. Therefore, the further the minima of the potential energy curves of the two electronic states are separated from each other, and the steeper the upper potential energy curve, the higher the v^E-value of the most probable transition from the $v^G=0$ state will be and the greater the variety of v^E states will be, among transitions to which the total transition probability is distributed[15].

As has been mentioned above, in the unhindered case, $\theta^G{}_{eq}=\theta^E{}_{eq}=0^\circ$. Therefore, in this case, the transition probability from the $v^G=0$ state will be concentrated mostly in the $0-0$ band. On the other hand, in the hindered case, $\theta^G{}_{eq} > \theta^E{}_{eq} > 0^\circ$, and the upper potential energy curve may be steeper than that in the unhindered case. Therefore, in this case, the transition probability from the $v^G=0$ state will be broadly distributed among transitions to a comparatively large number of v^E states.

The Shape of the Band.—From the considerations of both the distribution of the population of configurations in the electronic ground state and of the intensity distribution among transitions from the most probable vibrational state associated with the electronic ground state to various vibrational states associated with the electronic excited state, it is expected that, in the unhindered case, the absorption will occur over a comparatively narrow range of wavelengths and that the greater the steric hindrance, the wider the range of wavelengths over which the absorption will occur. Thus, as far as the twisting mode about the single bonds is concerned, it is expected that the absorption band will be broadened by the steric hindrance.

This expected effect of steric hindrance in broadening the absorption band may be of two kinds: (a) a broadening of the whole band system or (b) a broadening of individual absorption lines originating in the other kind of vibrational mode and, consequently, a blurring of the fine structure of the band.

The half-band-width, as well as the ratio of the integrated intensity or the oscillator strength to the intensity of the absorption maximum, may be taken as a measure of the broadness of the band as a whole. In Table I, instead of the half-band-width, the wave number interval between the absorption maximum and the point of half the intensity of the maximum at a longer wavelength than the maximum, which is referred to as $\varDelta\nu$, is presented, together with the $f_{\mathrm{exp}}/\varepsilon_{\mathrm{max}}$ ratio for each compound.

It seems that there is, in gross, a trend in conformity with the above expectations, although it is doubtful, because of uncertainty involved in the estimation of these data, whether much significance can be attached to this apparent trend. Thus, the effect of steric hindrance of broadening the band as a whole is not clear, although its possibility can not be excluded.

On the other hand, the effect of blurring the fine structure of the band and, eventually, of making the band structureless seems to be more convincing.

As was shown in Fig. 1 of Part V of this series, the conjugation band of *trans*-stilbene exhibits quite a well-resolved fine structure. The separations of the fine structure are about 1340 cm^{-1} at 20°C; these become 1480 cm^{-1} at -130°C[16]. The conjugation bands of *p*-phenylstilbene, *p, p'*-diphenylstilbene[1-IX] and styrene[4] exhibit a similar, though somewhat more blurred, fine structure. In contrast with the conjugation bands of these probably

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[15] See, for example: G. Herzberg, "Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules", 2nd ed., D. Van Nostrand Company, Inc., New York (1950), p. 193 ff.

[16] R. N. Beale and E. M. F. Roe, *J. Chem. Soc.*, **1953**, 2755.

unhindered compounds, the bands of probably nonplanar related compounds are almost perfectly structureless. (By the way, the conjugation band of biphenyl is structureless.)

According to Beale and Roe[16], the fine structure of the conjugation band of *trans*-stilbene is considered to originate in an ethylenic C=C stretching frequency. This bond undergoes the largest change in π-bond order on the excitation of the molecule; hence, the minima of the potential energy curves of the electronic ground state and of the electronic excited state for the stretching vibration of this bond are probably at values of the bond length considerably different from each other. (Since the π-bond order decreases on the excitation, the equilibrium bond length in the upper state is probably longer than that in the lower state.) Therefore, it must be possible for transitions from the lowest vibrational level of the electronic ground state to several vibrational levels of the electronic excited state to occur and, since the energy separations of the vibrational levels must be comparatively large, they will probably be revealed as the progression of the fine structure.

As has been mentioned above, the transition probability is considered to be concentrated in a considerably restricted wavelength range in the unhindered case, in so far as the twisting mode about the single bonds is concerned. Consequently, in this case, the progression originating in the C=C stretching mode is not so blurred and will reveal itself as a comparatively well-resolved fine structure.

On the other hand, in the case of hindered molecules, the transition probability is considered to be distributed among a greater variety of transitions covering a wider range of wavelengths; the fine structure will thereby be blurred. The same explanation will be applicable to the other systems.

Summary

The moment of the transition from the highest occupied orbital to the lowest vacant orbital has been calculated, by the simple LCAO MO method, as a function of the angle of the twist of the " single " bond for biphenyl, styrene and stilbene, each as a representative of alternant hydrocarbon systems. Thereby, it has been shown that the decrease in the intensity of the conjugation band observed with sterically hindered compounds, as compared with the band of the sterically unhindered parent compound, can be explained almost entirely satisfactorily by the decrease in the transition moment associated with the deviation of the most probable configuration of the molecule from the planarity. In this connection, Jaffé and Orchin's explanation, as well as Braude's explanation, of the steric hypochromic effect has been criticized.

From a consideration of the potential energy curves of the electronic ground state and of the electronic excited state for the twist of the "single" bond, an explanation has been suggested of the notable fact that the conjugation bands of sterically hindered stilbenes are almost structureless in contrast with the band of *trans*-stilbene, which has quite a well-resolved fine structure.

Department of Chemistry
College of General Education
The University of Tokyo
Meguro-ku, Tokyo