Relations between the Electronic Absorption Spectra and the Spatial Configurations of Conjugated Systems. XIII. Phenyl-carbonyl and Vinyl-carbonyl Systems

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As is well known, Braude[1] classified the steric effects in the ultraviolet absorption spectra of conjugated compounds into two types. Type 1, exemplified by the substituted phenyl- and vinyl-carbonyl compounds, is characterized by a decrease in the absorption intensity alone, with no appreciable accompanying change in the position of the absorption maximum. Type 2, exemplified by the *o*-alkylated biphenyls, is characterized by a hypsochromic shift as well as by a decrease in the absorption intensity.

Braude ascribed the difference between the two types to the difference in the underlying mechanism. According to him, while the type 2 effect occurs when the steric hindrance to the planarity of the conjugated system is relatively strong, the type 1 effect occurs when the steric hindrance is relatively weak, and while in the former case the maximum absorption originates in electronic transitions in those molecules with the most probable non-planer configuration in the electronic ground state, in the latter case it originates in transitions in those molecules with the less probable planar or near-planar configuration in the ground state. He therefore ascribed the decrease in the intensity of the absorption maximum in the case of type 1 to the decrease in the population ratio, r, of the planar or near-planar configuration in the electronic ground state (i. e., the probability in which molecules in the electronic ground state assume the planar or near-planar configuration); further, he assumed that the population ratio, r, and hence the molar extinction coefficient of the absorption maximum, ε, would be proportional to $\cos\theta$, where θ is the interplanar angle between moieties of the conjugated system linked to each other by a formally single bond, i. e., the angle of twist of the bond, in the most probable configuration[2,3]. Afterwards[4,5], he replaced the cosine of θ in the above assumption by the cosine-square of θ; that is, he assumed the following relation:

$$\varepsilon/\varepsilon_0=\cos^2\theta \qquad (1)$$

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[1] E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, **1949**, 1890.

[2] E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).

[3] E. A. Braude and E. S. Waight, in W. Klyne, "Progress in Stereochemistry, I", Butterworths Scientific Publications, London (1954), p. 126.

[4] E. A. Braude, in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods", Academic Press, Inc., New York (1955), p. 131.

[5] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, **1955**, 3754.

where ε_0 is the molar extinction coefficient of the absorption maximum of the sterically unhindered reference compound.

As has been mentioned in Parts XI⁶⁾ and XII⁷⁾ of this series, Braude's interpretation of steric effects is unacceptable. Although the border line between the two types of steric effect is not distinct in practice, the classification may be provisionally admitted. However, the difference between the two types is due neither to a difference in the underlying mechanism nor to a difference in the magnitude of steric hindrance. The sensibility of the transition energy to a change in the spatial configuration of the conjugated system depends on the nature of the electronic upper state to which the transition leads. According to Murrell⁸⁾, the energy of the transition to a perturbed, locally-excited state is relatively sensitive to a change in the configuration, while, on the other hand, that of the transition to a perturbed, intramolecular electron-transfer state is relatively insensitive. Roughly, it may be said that the steric effect in the former case corresponds to type 2, and that in the latter case to type 1. At any rate, in both cases, the maximum absorption is considered to originate in transitions in those molecules with the most probable configuration in the electronic ground state, contrary to the theory of Braude.

In this way, the untenability of the theory of Braude may be said to have been established. However, Eq. 1 itself, assumed by Braude on the wrong grounds, seems to have some plausibility. Thus, the values of θ calculated by the use of this relation for some benzaldehydes and acetophenones are generally in quite good agreement with the values deduced from the dipole moment data, although the latter values themselves seem also to be unreliable, because their deduction was based on a rather arbitrary assumption bearing a certain similarity to Eq. 1. Furthermore, a relation similar to Eq. 1 was found by Klevens and Platt⁹⁾ to hold in the case of *o*-substituted dimethylanilines. Thus, according to them, the oscillator strength, f, of each band varies with the cosine-square of the minimum angle of twist of the dimethylamino group with respect to the benzene ring estimated from the van der Waals radius of the ortho substituent.

It may, therefore, be of some interest to examine to what extent the relation assumed by Braude can be validated by theoretical considerations. In the present paper, with special emphasis on this problem, it is attempted, on the same ground as in the previous papers of this series, to clarify the relation between the conjugation band and the spatial configuration of the conjugated system in the cases of the phenyl-carbonyl (C_6-C=O) and vinyl-carbonyl (C=C-C=O) systems as representatives of systems exhibiting the so-called type 1 steric effect.

Transition Energy as a Function of the Angle of Twist

It has already been pointed out by Nagakura and Tanaka¹⁰⁻¹²⁾ that the intense band near 240 mμ, i. e., the conjugation band, of acetophenones as well as of benzaldehydes has the nature of an intramolecular electron-transfer band. According to them, the band is due to electronic transition between two π-orbitals, ψ_{-1} and ψ_{+1}, which arise primarily from the interaction of the lowest antibonding π-orbital of the carbonyl group, $\phi_{-1(C)}$, and the highest bonding π-orbital of the benzene ring, $\phi_{+1(B)}$. Since the interaction of two orbitals is always in the sense of a repulsion, the energy separation between ψ_{-1} and ψ_{+1} will become greater as the interaction between $\phi_{-1(C)}$ and $\phi_{+1(B)}$ becomes greater. Therefore, this theory leads to a surmise that the steric hindrance to coplanarity of the benzene nucleus and the carbonyl group would result in a bathochromic shift of the band. As was pointed out in Part X¹³⁾ of this series, this surmise is contrary to observed facts. Thus, with the acetophenone system, the steric effect should be considered to cause a hypsochromic shift of the band. It is evident that the omission of interactions among orbitals other than $\phi_{-1(C)}$ and $\phi_{+1(B)}$ is an over-simplification. Therefore, in the first place, the dependence of the transition energy on the angle of twist of the formally single bond is examined by the use of the perturbation theory, all the π-orbitals being taken into account.

Notation.—A conjugated system is represented by R-S and is regarded as being composed of two mesomeric systems, R and S, linked to each other by a formally single bond between the atoms r and s, which belong to R and S respectively. In the phenyl-carbonyl and vinyl-carbonyl systems, R represents the benzene nucleus or the ethylenic bond and S represents the carbonyl bond.

The following notation is used: ϕ_m: m-th MO of R. $\phi_{n'}$: n'-th MO of S. ψ_k: k-th

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6) H. Suzuki, This Bulletin, **33**, 619 (1960).
7) H. Suzuki, ibid., **35**, 1715 (1962).
8) J. N. Murrell, *J. Chem. Soc.*, **1956**, 3779.
9) H. B. Klevens and J. R. Platt, *J. Am. Chem. Soc.*, **71**, 1714 (1949).
10) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954).
11) J. Tanaka, S. Nagakura and M. Kobayashi, ibid., **24**, 311 (1956).
12) J. Tanaka and S. Nagakura, ibid., **24**, 1274 (1956).
13) H. Suzuki, This Bulletin, **33**, 613 (1960).

MO of R–S. $F_m=\alpha-v_m\beta$: energy of ϕ_m. $F_{n'}=\alpha-v_{n'}\beta$: energy of $\phi_{n'}$. $E_k=\alpha-w_k\beta$: energy of ψ_k. χ_i: AO of atom i. $b_{m,r}$: coefficient of χ_r in ϕ_m. $b_{n',s}$: coefficient of χ_s in $\phi_{n'}$. $c_{k,i}$: coefficient of χ_i in ψ_k. $p_{k,i-j}=c_{k,i}c_{k,j}$: partial π-bond order of the i–j bond in ψ_k, i. e., the contribution to the π-bond order of the bond by an electron occupying ψ_k. $\alpha_i=\alpha+\delta_i\beta$: coulomb integral of χ_i. $\rho_{i-j}\beta$: resonance integral between χ_i and χ_j.

By the way, α is the coulomb integral of the 2 pπ atomic orbital of a carbon atom, and β is the resonance integral of the 2 pπ atomic orbitals of adjacent carbon atoms in the benzene ring. That is, v or w represents the energy of the orbital in a unit of $-\beta$ relative to the energy of the 2 pπ atomic orbital of a carbon atom.

In each of the mesomeric systems, the highest bonding π-orbital is designated as $+1$, and the lower orbitals in the order of decreasing energy are designated as $+2$, $+3$, and so on. Quite analogously, the lowest antibonding π-orbital is designated as -1, and the higher orbitals in the order of increasing energy are designated as -2, -3, and so on. Thus, for example, ϕ_{+1}, $\phi_{+1'}$, and ψ_{+1} refer to the highest bonding π-orbitals of R, S, and R–S respectively.

The parameter ρ_{i-j} can be expressed as follows, on the basis of the usual assumption of the proportionality of the resonance integral to the overlap integral:

$$\rho_{i-j}=\cos\theta_{ij}\cdot S(R_{i-j},0°)/S(\text{benz.}) \tag{2}$$

In this expression, θ_{ij} is the angle of twist of the bond (i. e., the angle by which the axes of χ_i and χ_j are twisted with respect to each other), R_{i-j} is the length of the bond, $S(R_{i-j}, 0°)$ is the overlap integral of χ_i and χ_j when the interatomic distance is R_{i-j} and the angle of twist is 0°, and S(benz.) is the π–π overlap integral for adjacent carbon atoms in the benzene nucleus.

Classification of Conjugated Systems.—With respect to the heights of the energies of $\phi_{-1'}$ and $\phi_{+1'}$ relative to the energies of ϕ_{-1} and ϕ_{+1}, the following three typical cases are distinguished:

(A) $v_{-1}=v_{-1'}$; $v_{+1}=v_{+1'}$

(B) $v_{-1}<v_{-1'}$; $v_{+1}>v_{+1'}$

(C) $v_{-1}>v_{-1'}$; $v_{+1}>v_{+1'}$

These cases are exemplified by the following conjugated systems: (A), butadiene and biphenyl; (B), styrene; and (C), phenyl-carbonyl and vinyl-carbonyl.

In the case of A, ψ_{-1} and ψ_{+1} are regarded as orbitals arising from the perturbation of $1/\sqrt{2}\cdot(\phi_{-1}+\phi_{-1'})$ and of $1/\sqrt{2}\cdot(\phi_{+1}-\phi_{+1'})$ respectively, and the transition from ψ_{+1} to ψ_{-1} corresponds to the transition to a so-called charge-resonance state[14]. In the case of B, ψ_{-1} and ψ_{+1} are regarded as originating from ϕ_{-1} and ϕ_{+1} respectively, and the transition from ψ_{+1} to ψ_{-1} is the transition to a so-called perturbed, locally-excited state.

In general, the π-orbitals in any even-alternant hydrocarbon system occur in pairs. Thus, for such a system, $v_{+m}=-v_{-m}$, and $|b_{+m,i}|=|b_{-m,i}|$. Therefore, any system in which both fragments, R and S, are even-alternant hydrocarbon systems belongs to either case A or case B; moreover, in such a system, not only in case A but also in case B, the interaction of ϕ_{-1} with $\phi_{-1'}$ and that of ϕ_{+1} with $\phi_{+1'}$ make predominant contributions to the formation of ψ_{-1} and of ψ_{+1} respectively. Accordingly, as the value of ρ_{r-s} becomes larger, the energies of ψ_{-1} and ψ_{+1} become lower and higher respectively, and, consequently, the energy separation between them becomes smaller. This means that a deviation from coplanarity of R and S by a twist of the formally single r–s bond in any even-alternant hydrocarbon system, R–S, results in a hypsochromic shift of the conjugation band. In particular, in case A, the interaction of ϕ_{-1} with ϕ_{-1}, as well as that of ϕ_{+1} with $\phi_{+1'}$, depends on the ρ_{r-s} in the first order. Therefore, in this case, the transition energy increases to a first approximation linearly with the decreasing value of ρ_{r-s}. Representative alternant hydrocarbon systems have been discussed in some detail in the preceding parts of this series.

In case C, the transition from ψ_{+1} to ψ_{-1} corresponds to the transition to a perturbed electron-transfer state. The present paper is concerned chiefly with this case.

Treatment of Case C by Means of the Perturbation Theory.—In case C, ψ_{-1} and ψ_{+1} are regarded as orbitals arising from the perturbation of $\phi_{-1'}$ and ϕ_{+1} respectively, interaction between ϕ_m's and $\phi_{n'}$'s being regarded as a pertubation. Thus, if the $|A_{m,n}\ \rho_{r-s}|\ll 1$ relation holds for each pair of orbitals of R and S, where $A_{m,n'}=b_{m,r}b_{n',s}/(v_m-v_{n'})$, the first order perturbation theory gives the following expressions for ψ_{-1} and ψ_{+1}:

$$\psi_{-1}=N_{-1}(\phi_{-1'}-\sum_m A_{-1',m}\,\rho_{r-s}\,\phi_m) \tag{3}$$

$$\psi_{+1}=N_{+1}(\phi_{+1}-\sum_{n'} A_{+1,n'}\,\rho_{r-s}\,\phi_n) \tag{4}$$

where N_{-1} and N_{+1} are normalization factors. The second order approximation to the energy of these orbitals is given by:

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[14] J. N. Murrell, *Quart. Revs.*, 15, 191 (1961).

$$w_{-1}=v_{-1'}+\sum_{m} G_{-1',\,m}\,\rho^2{}_{\mathrm{r-s}} \equiv v_{-1'}+g_{-1}\,\rho^2{}_{\mathrm{r-s}} \qquad (5)$$

$$w_{+1}=v_{+1}+\sum_{n'} G_{+1,\,n'}\,\rho^2{}_{\mathrm{r-s}} \equiv v_{+1}+g_{+1}\,\rho^2{}_{\mathrm{r-s}} \qquad (6)$$

where $G_{m,n'}=b^2{}_{m,\mathrm{r}}b^2{}_{n',\mathrm{s}}/(v_m-v_{n'})$. Accordingly, the energy separation between ψ_{-1} and ψ_{+1}, $\Delta E_{-1,\,+1}$(in $-\beta$), is expressed as:

$$\Delta E_{-1,\,+1}=\Delta w_{-1,\,+1}=\Delta v_{-1',\,+1}+\Delta g_{-1,\,+1}\,\rho^2{}_{\mathrm{r-s}}$$

where $\Delta v_{-1',\,+1}$ and $\Delta g_{-1,\,+1}$ represent $v_{-1'}-v_{+1}$ and $g_{-1}-g_{+1}$ respectively. (The subscript -1, $+1$, which refers to quantities concerning the transition from ψ_{+1} to ψ_{-1}, is subsequently omitted for the sake of brevity.) The partial π-bond orders are given by:

$$p_{-1,\,\mathrm{r-s}}=-g_{-1}\,\rho_{\mathrm{r-s}}\,N^2{}_{-1}$$

$$p_{+1,\,\mathrm{r-s}}=-g_{+1}\,\rho_{\mathrm{r-s}}\,N^2{}_{+1}$$

The change in the π-bond order of the r–s bond on the one-electron transition from ψ_{+1} to ψ_{-1}, $\Delta P_{\mathrm{r-s}}$, is $p_{-1,\,\mathrm{r-s}}-p_{+1,\,\mathrm{r-s}}$.

When R is an alternant hydrocarbon system, and when $v_{-1'}$ is positive, $-G_{-1',\,-m}$ is greater than $G_{-1',\,+m}$; that is, the contribution of the antibonding orbitals of R to ψ_{-1} is greater than that of the bonding orbitals of R. In this case, g_{-1} is negative, and $p_{-1,\,\mathrm{r-s}}$ is positive.

S is taken to represent an unsaturated group, C=X, in which X may represent a hetero-atom such as oxygen or nitrogen. The coulomb integral of the pπ atomic orbital of atom X, α_{X}, is expressed as $\alpha+\delta_{\mathrm{X}}\beta$. As may easily be proved, according as $\delta_{\mathrm{X}} \lesseqgtr -v_{+1}$, $-G_{+1,\,-1'} \lesseqgtr G_{+1,\,+1'}$, and, consequently, $g_{+1} \gtreqless 0$ and $p_{+1,\,\mathrm{r-s}} \gtreqless 0$. Thus, if δ_{X} is smaller than $-v_{+1}$, the contribution of ϕ_{+1} to $\psi_{+1'}$ as a perturbed orbital of ϕ_{+1} surpasses that of $\phi_{-1'}$. As δ_{X} becomes greater, the contribution of $\phi_{+1'}$ decreases owing to an increase in the energy separation of $v_{+1}-v_{+1'}$ as well as to a decrease of $b_{+1',\,\mathrm{s}}$, and the contribution of $\phi_{-1'}$ increases owing to a decrease in the energy separation of $v_{-1'}-v_{+1}$ as well as to an increase of $b_{-1',\,\mathrm{s}}$. This situation may be stated in terms of the resonance theory as follows: With the increasing value of δ_{X}, the contribution of the ionic structure, $\mathrm{R^+{=}S^-}$, to the electronic ground state increases, resulting in an increase of the π-bond order of the r–s bond in the state.

Putting the above discussions together, the situation can be expressed as follows. If $\delta_{\mathrm{X}} \leqslant -v_{+1}$, Δg is negative and $\Delta P_{\mathrm{r-s}}$ is positive. In this case, a decrease in $\rho_{\mathrm{r-s}}$ results in an increase in Δw. This means that a twist of the r–s bond will cause a hypsochromic shift of the absorption band due to the transition from ψ_{+1} to ψ_{-1}. Of course, the smaller the value of δ_{X}, the larger the absolute value of Δg and, hence, the more effective the steric hypsochromic effect. The extreme case in which δ_{X} is zero reduces to case A or B. If δ_{X} has a moderately larger value than $-v_{+1}$, Δg may be nearly zero. In this case, a steric distortion will result in substantially no shift of the band. In the case where δ_{X} is much larger than $-v_{+1}$, Δg is positive and, accordingly, a twist of the bond will cause a bathochromic shift of the band.

Calculation and Discussion.—The length of the carbonyl bond in a number of compounds has an average value of 1.23±0.01 Å[15]. By the use of the value of 1.23 Å, the ρ-value for this bond is estimated at 0.844.

In the $\mathrm{C_6}$–C=O and the C=C–C=O systems, the r–s bond is the 1–1′ bond linking the carbonyl group to the phenyl or the vinyl group. The length of this bond, $R_{1-1'}$, is assumed for the sake of convenience to be 1.48 Å when the angle of twist of the bond, $\theta_{1,\,1'}$, is 0°. Then the value of $\rho_{1-1'}$ is 0.858 when $\theta_{1,\,1'}$ is 0°, and the same relation among ρ, θ, and R as the one assumed tentatively for the cases of styrene[6] and biphenyl[16] can be used.

In application of the perturbation theory, the forms of ϕ's and the values of v's obtained by the simple LCAO MO method were used. When R is the benzene ring, for example, $v_{-1}=-v_{+1}=1$, and $b_{-1,\,1}=b_{+1,\,1}=1/\sqrt{3}$. By the way, in the C=C–C=O system, the δ-value for the ethylenic bond was taken to be 1.080, as in the cases of butadiene[7], styrene[6] and stilbene[17].

In Fig. 1, the following quantities as functions of δ_{X} for the $\mathrm{C_6}$–C=X system, calculated by the use of th above parameter values, are

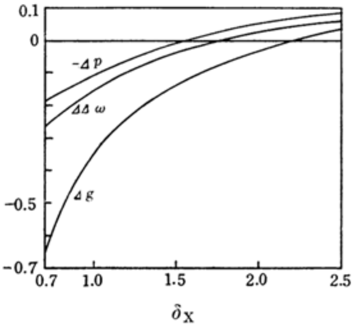

Fig. 1. $\Delta P_{\mathrm{r-s}}$, $\Delta\Delta w$, and Δg as functions of δ_{X} in the $\mathrm{C_6}$–C=X system.

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[15] "Tables of Interatomic Distances and Configuration in Molecules and Ions", The Chemical Society, London (1958).

[16] H. Suzuki, This Bulletin, 32, 1340 (1959).

[17] H. Suzuki, ibid., 33, 379 (1960).

shown graphically: the value of Δg calculated from Eqs. 5 and 6; the difference between the value of Δw at $\theta_{rs}=0°$ and the value at $\theta_{rs}=90°$, $\Delta\Delta w$, and the value of ΔP_{r-s} at $\theta_{rs}=0°$, calculated by an application of the simple LCAO MO method to the whole conjugated system. The foregoing trends of the dependence of a change in the transition energy associated with a change in the angle of twist of the pivot bond, and of the change in the π-bond order of the bond, on the transition on the value of δ_X are clearly shown. In the case of C=C–C=X, the situation is quite similar.

After Matsen[18], the α/β ratio is assumed to be about 2.4. Then, on the basis of the assumption that the value of α_X should be proportional to the ionization energy of an electron occupying the pπ atomic orbital in the pertinent valence state of atom X, the value of δ for the 2pπ orbital of oxygen is estimated at 1.27, by the use of the ionization energy data collected by Pritchard and Skinner[19]. Of course, this numerical value is not conclusive, but approximately this value, probably 1.2∼1.3, seems to be pertinent. (By the way, the value of δ for the 2pπ orbital of nitrogen is estimated at 0.60 by a similar procedure.)

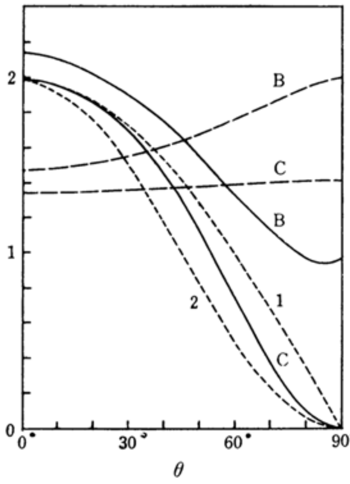

Fig. 2. The transition energy (in $-\beta$), Δw, and the dipole strength of the transition (in Å^2), M^2, as functions of the angle of twist of the formally single bond, θ, in the phenyl-carbonyl system as well as in the styrene system.

Broken lines, Δw; Solid lines: M^2;
B, C_6–C=C; C, C_6–C=O
Dotted lines: 1, $M^2(0°)\cdot\cos\theta$;
2, $M^2(0°)\cdot\cos^2\theta$

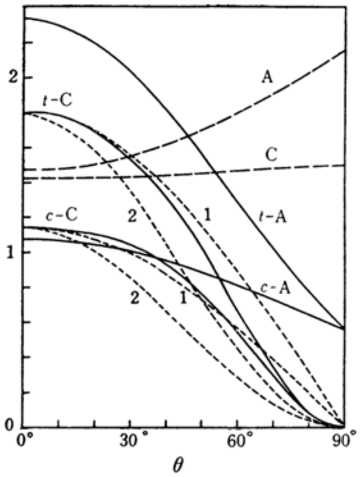

Fig. 3. The transition energy (in $-\beta$), Δw, and the dipole strength of the transition (in Å^2), M^2, as functions of the angle of twist of the formally single bond, θ, in the vinyl-carbonyl system as well as in the butadiene system.

Broken lines, Δw; Solid lines, M^2;
A, C=C–C=C; C, C=C–C=O
t, s-trans; *c*, s-cis.
Dotted lines: 1, $M^2(0°)\cdot\cos\theta$;
2, $M^2(0°)\cdot\cos^2\theta$

When δ_X is 1.2∼1.3, Δg, as well as $\Delta\Delta w$, has a small negative value. This means that a deviation from planarity of the conjugated system, of C_6–C=O as well as of C=C–C=O, will cause a small hypsochromic shift of the socalled conjugation band, in accordance with observations.

In Figs. 2 and 3, the Δw values for $\delta_X=1.3$, calculated by the simple LCAO MO method for the phenyl-carbonyl and vinyl-carbonyl systems, are plotted against θ_{rs} with broken lines. In these figures, the corresponding curves for the styrene and the butadiene system are also shown for the sake of comparison.

If X is N instead of O, the steric hypsochromic shift will be somewhat more effective, δ_N being smaller than δ_O. Experimental data pertinent to test this surmise is not available. However, for example, the fact that the steric hypsochromic effect in the case of the semicarbazones of acetophenones is appreciably more effective than in tha case of acetophenones[5] seems to suggest the validity of this surmise.

According to Heilbronner and Gerdil[20], the weak longest-wavelength band at 546 mμ (ε_{max} =440) (A-band) of 1-acetylazulene undergoes a bathochromic shift as well as a reduction of intensity by substitution of a methyl group

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[18] F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
[19] H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955).
[20] E. Heilbronner and R. Gerdil, *Helv. Chim. Acta*, **39**, 1996 (1956).

at the 2- or the 8-position of the azulene nucleus, which will prevent the coplanar arrangement of the azulene nucleus and the carbonyl group. This band has been considered to correspond to the α-band ($\lambda_{\max}=580\,\mathrm{m}\mu$; $\varepsilon_{\max}=329$) of azulene, and the latter has been assigned as a band due to the $\mathrm{N}\rightarrow\mathrm{V}_1$ transition[21]. Thus, if R and S are taken to refer to the azulene nucleus and the carbonyl group respectively, the $v_{-1}<v_{-1'}$ and $v_{+1}>v_{+1'}$ relations probably exist, and the A-band of the 1-acetylazulenes may be regarded as a band due to the transition from ψ_{+1} as a perturbed orbital of ϕ_{+1} to ψ_{-1} as a perturbed orbital of ϕ_{-1}. The transition may be said to be one to a perturbed locally-excited state, and the situation may be considered to belong to case B. Therefore, a bathochromic effect of a twist of the bond linking the azulene nucleus and the carbonyl group to each other would be rather surprising. Heilbronner and Gerdil correlated this effect to a possible decrease in the π-bond order of the bond upon excitation. This effect can be interpreted as below on the basis of the above considerations.

According to Pariser[22], the energies of the lowest vacant and the highest occupied orbital of azulene and the coefficients of the $2\mathrm{p}\pi$ atomic orbital χ_1 in these orbitals in the simple LCAO MO approximation are as follows: $v_{-1}=+0.40039$, $v_{+1}=-0.47726$; $b_{-1,1}=0.06321$, $b_{+1,1}=0.54285$. On the other hand, if the values $\delta_{\mathrm{O}}=1.3$ and $\rho=0.844$ are used for the carbonyl bond, the following values are obtained: $v_{-1'}=+0.415$, $v_{+1'}=-1.715$; $b_{-1',1'}=0.897$, $b_{+1',1'}=0.441$. Thus, since $-v_{+1}$ is smaller than δ_{O}, g_{+1} is negative. That is, of the effects of the two orbitals of the carbonyl group on ϕ_{+1}, the depressing effect of $\phi_{-1'}$ outweighs the raising effect of $\phi_{+1'}$. In addition, since $b_{+1,1}$ is much larger than $b_{-1,1}$, $|G_{+1,-1'}|$ is larger than $|G_{-1,-1'}|$, notwithstanding the fact that the energy separation of $v_{-1'}-v_{+1}$ is larger than that of $v_{-1'}-v_{-1}$. That is, the depression of the energy of ϕ_{+1} due to the interaction with $\phi_{-1'}$ is probably greater than that of ϕ_{-1}. Thus, the energy separation between ψ_{-1} as a perturbed orbital of ϕ_{-1} and ψ_{+1} as a perturbed orbital of ϕ_{+1} will become greater as the $\rho_{1-1'}$ parameter becomes greater.

Absorption Intensity as a Function of the Angle of Twist

The moment of the one-electron transition from ψ_{+1} to ψ_{-1} is denoted by $M_{-1,+1}$, which is subsequently abbreviated to M, the subscript being omitted. In the case of C, on the basis of Eqs. 3 and 4, the square of this transition moment, i. e., the dipole strength of the transition, can be expressed as follows:

$$\begin{aligned}M^2&=2\left(\int\psi_{-1}\,q\,\psi_{+1}\,\mathrm{d}\tau\right)^2\\&=2\,\rho^2{}_{\mathrm{r-s}}\,N^2{}_{-1}\,N^2{}_{+1}\\&\qquad\times\Big(\sum_m A_{-1',m}\,I_{+1,m}\\&\qquad+\sum_{n'} A_{+1,n'}\,I_{-1',n'}\Big)^2\end{aligned}$$

where $I_{m,n}$ represents the integral $\int\phi_m\,q\,\phi_n\,\mathrm{d}\tau$, q being a general symbol for the position coordinate of the electron. To a first approximation, $I_{m,n'}=0$. Accordingly, when $\rho_{\mathrm{r-s}}$ is zero, M^2 is zero.

If the assumption is made that N_{-1}, N_{+1}, and I's do not vary in magnitude to any appreciable extent with changes in the value of $\rho_{\mathrm{r-s}}$, the oscillator strength, f, can be considered to be approximately proportional to $\rho^2{}_{\mathrm{r-s}}$, since Δw, and hence $\nu_{\max}$, are comparatively insensitive to a change in the value of $\rho_{\mathrm{r-s}}$. Further, if it is assumed that the length of the pivot bond remains unchanged when the angle of twist of the bond, θ_{rs}, does vary, $\rho_{\mathrm{r-s}}$ can be taken to be proportional to $\cos\theta_{\mathrm{rs}}$; hence, the oscillator strength can be considered to be proportional to $\cos^2\theta_{\mathrm{rs}}$. Furthermore, if the molar extinction coefficient at the absorption maximum can be taken to be proportional to the oscillator strength of the band, its proportionality to the cosine-square of the angle of twist, i. e., the relation assumed by Braude, is reached.

It should be noted that many assumptions have been needed to reach this relation by the present approach. Above all, the assumption of the insensibility of $N_{-1}\,N_{+1}$ to $\rho_{\mathrm{r-s}}$ seems not to be permissible. Accordingly, insofar as it depends on the present approach based on the perturbation theory, the relation of Braude can be admitted only as a very rough approximation.

The dipole strength of the transition as a function of θ_{rs} has been calculated for the phenyl-carbonyl system, as well as for the vinyl-carbonyl system, by taking the value of δ_{O} to be 1.3 and by applying the simple LCAO MO method to the whole conjugated system. In these calculations, all the valence angles at carbon atoms have been assumed to be 120°. In Figs. 2 and 3, the results of the calculation are shown graphically with solid lines, together with the analogous data for the styrene and butadiene systems for the sake of comparison.

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[21] C. A. Coulson, *Proc. Phys. Soc.*, 65, 933 (1952).

[22] R. Pariser, *J. Chem. Phys.*, 25, 1112 (1956).

It is seen that the transition probability of the electron-transfer band of the phenyl-carbonyl system, as well as of the vinyl-carbonyl system, is slightly more sensitive to the steric hindrance than that of the conjugation band of the corresponding conjugated hydrocarbon system.

By the way, the calculated values (in Å^2) of M^2 at $\theta=0°$, i.e., $M^2(0°)$, are as follows: C_6–C=O, 1.984; C=C–C=O, s-trans, 1.794; s-cis, 1.140. The prefix s denotes that the steric arrangement is about the formally single bond between the ethylenic bond and the carbonyl bond. From the value of $M^2(0°)$, the oscillator strength (the f_{theor}-value) for the planar phenyl-carbonyl system, for example, is calculated to be 0.909. This value is to be compared with the f_{exp}-value of 0.310 for benzaldehyde estimated from the absorption curve reported in Part X$^{13)}$ of this series. In this case, the ratio of f_{theor} to f_{exp} is 2.93, a value which is reasonable in view of the general trend of this ratio observed for some conjugated hydrocarbons in Part XII$^{7)}$ of this series.

In Figs. 2 and 3, curves for $M^2(0°)\cdot\cos\theta$ and $M^2(0°)\cdot\cos^2\theta$ are also shown with dotted lines. It is seen that, for each system, the $M^2(\theta)$ curve lies between the cosine curve and the cosine-square curve, largely approaching the former.

As was mentioned in Part XII of this series, however, there seems to be a trend, the smaller the f-value, for the ratio of f_{theor} to f_{exp} to be slightly the greater, and also a trend, the greater the most probable angle of twist, for the ratio of f_{exp} to the molar extinction coefficient at the absorption maximum, $\varepsilon_{\max}$, to be the greater. If these trends can be considered as holding in general, it may be expected that the value of $\varepsilon_{\max}$ decreases somewhat more rapidly with an increasing value of θ than would be anticipated from the calculated value of $M^2(\theta)$. Therefore, it is not imposible thet $\varepsilon_{\max}$ is approximately proportional to $\cos^2\theta$ rather than to $\cos\theta$.

Thus, it may be said that the relation, proposed by Braude on a quite unreasonable ground, has been given a theoretical support here to some extent. At any rate, such a relation should, of course, be considered to be a rough approximation, since it is an approximation to correlate the observed ε-value or the f_{exp}-value with the steric effect alone, neglecting the possible hyperchromic effect of an electronic origin of the substituent and the uncertainty of the values due to the probably poor resolvability of the band concerned from the neighboring bands.

Summary

It has been shown that the characteristic feature of the steric effect on the conjugation band in the case of the phenyl-carbonyl and vinyl-carbonyl systems, i.e., the relatively small hypsochromic shift and the relatively large decrease in the intensity of the band, as compared with that in the case of the conjugated hydrocarbon systems, can be adequately interpreted using the simple MO approach. From theoretical considerations it has especially been concluded that the proportionality of the intensity of the band to the cosine-square of the angle of twist of the formally single bond in these systems, formerly assumed by Braude, may be admitted as a rough approximation in spite of the invalidity of its original reasoning.

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