A Theoretical Study on Biradicals. I. Theoretical Characteristics of Biradicals

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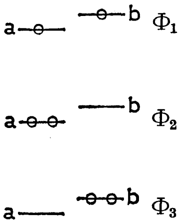
An interpretation is given on the characteristics of biradicaloids, such as the bonding, polar, and biradical characters of singlet biradicals. Systematization of the reactivity of singlet and triplet biradicals is based on the principle that 1) deformation takes place in the direction of bonding in singlet biradicals, and 2) deformation or bond formation occurs to separate unpaired-electrons from each other in triplet biradicals. Combination of the two principles is applied to the theory of orientation and stereoselection in excited-state reactions.

The word "biradical" in a chemical sense makes us think of a species having an odd electron on each of two sites of a molecule. This conforms to the interpretation of a biradical in the triplet state. However, problems may arise in the case of a singlet biradical.

The conversion of biradical species along the path of ground- and excited-state reactions has been treated theoretically.[1–4] Salem *et al.* discussed the nature of a singlet biradical by taking ionic states into account and explained a number of experimental results in regard to various reaction intermediates in photochemistry.[5–10] The present paper gives some new material.

Stabilization of Singlet Biradical by a Correlated Motion of Electrons

Consider a pair of two independent normalized one-electron space functions a and b whose overlap integral is s. In the case of biradical problems these two orbitals can be made to represent the two "unpaired"-electron orbitals essentially localized at each radical site. The following three configurations are here taken into consideration to treat the problem as a two-electron system:



$$\left.\begin{aligned}\Phi_1(1,2) &= \frac{1}{\sqrt{2+2s^2}}\{a(1)b(2)+b(1)a(2)\}\\ \Phi_2(1,2) &= a(1)a(2)\\ \Phi_3(1,2) &= b(1)b(2)\end{aligned}\right\} \quad (1)$$

It is assumed that orbitals a and b are real and their signs are chosen in such a way that s becomes positive.

The electronic states of this two-electron system are then given by

$$\Psi = \frac{1}{\sqrt{N}}(C_1\Phi_1+C_2\Phi_2+C_3\Phi_3), \quad (2)$$

where C_1, C_2, and C_3 can be obtained by solving the eigenvalue problem of the Hamiltonian matrix, and $1/\sqrt{N}$ is the normalization factor. They are the usual energy-extremized wave functions in which the effect of correlation in electron motion is taken into account.

Direct consideration of the correlated motion of electrons might also be considered. The extent of correlation in orbital motion could roughly be represented by the averaged reciprocal interelectronic distance,

$$\overline{\frac{1}{r_{12}}} = \frac{2}{\nu(\nu-1)}\iint\rho(1,2|1,2)\frac{1}{r_{12}}\mathrm{d}v(1)\mathrm{d}v(2), \quad (3)$$

(ν: number of electrons)

where r_{12} is the distance of electrons 1 and 2, and

$$\rho(1',2'|1,2) = \frac{\nu(\nu-1)}{2}\int\Psi^*(r_1'\sigma_1, r_2'\sigma_2, r_3\sigma_3, \cdots)\times\Psi(r_1\sigma_1, r_2\sigma_2, r_3\sigma_3, \cdots)\mathrm{d}\sigma_1\mathrm{d}\sigma_2\mathrm{d}r_3\mathrm{d}\sigma_3\cdots \quad (4)$$

is the second-order spinless density matrix. For the present two-electron problem, we have

$$\gamma \equiv \overline{\frac{1}{r_{12}}} = \iint\Psi^*(1,2)\frac{1}{r_{12}}\Psi(1,2)\mathrm{d}v(1)\mathrm{d}v(2). \quad (5)$$

The extremization of $\overline{1/r_{12}}$ is achieved by obtaining the stationary values satisfying

$$\delta\gamma = 0. \quad (6)$$

The variation with respect to C_1, C_2, and C_3 leads to the secular equation

$$\begin{vmatrix}\gamma_{11}-\gamma & \gamma_{12}-S_{12}\gamma & \gamma_{13}-S_{13}\gamma\\ \gamma_{21}-S_{21}\gamma & \gamma_{22}-\gamma & \gamma_{23}-S_{23}\gamma\\ \gamma_{31}-S_{31}\gamma & \gamma_{32}-S_{32}\gamma & \gamma_{33}-\gamma\end{vmatrix} = 0, \quad (7)$$

where

$$\gamma_{jk} = \iint\Phi_j^*(1,2)\frac{1}{r_{12}}\Phi_k(1,2)\mathrm{d}v(1)\mathrm{d}v(2)$$

and

$$S_{jk} = \iint\Phi_j^*(1,2)\Phi_k(1,2)\mathrm{d}v(1)\mathrm{d}v(2)$$

(j, k=1, 2, and 3).

The coefficient of Φ_j in Eq. 2 can be obtained simultaneously, giving correlation-extremized wave functions $\{\Psi^{(i)}\}$ which are always mutually orthogonal. Both energy-extremization and correlation-extremization give wave functions with an essentially parallel trend in nonpolar species.[11] Thus in such favourable cases, we can use correlation-extremized wave functions as an approximate substitute of the usual energy-extremized functions. Such a consideration of the interaction of at least three configurations as mentioned above is essential in the theoretical interpretation of biradicals.

Bonding Character between Two Radical Sites

The bonding character between two radical sites each containing essentially one electron can be discussed by using Ψ of Eq. 2. A most reasonable scale of bonding character[12] might be the magnitude of accumulation of electron population in the intermediate region between two radical sites.[13–15]

The distribution of electron density is given by

$$\rho(1) = 2\int\Psi^*(1,2)\Psi(1,2)\mathrm{d}v(2). \tag{8}$$

The density $\rho(1)$ is divided into three terms as

$$\rho(1) = A_{11}a(1)^2 + 2A_{12}a(1)b(1) + A_{22}b(1)^2. \tag{9}$$

The bonding strength can be determined by the second term of r.h.s. since the coefficient A_{12} of the cross term $a(1)b(1)$ contributes to the accumulation of electrons in the intermediate region.

It follows from Eq. 2 that

$$A_{12} = \frac{1}{N}\left\{\frac{s}{1+s^2}C_1{}^2 + \sqrt{\frac{2}{1+s^2}}C_1(C_2+C_3) + 2sC_2C_3\right\}, \tag{10}$$

where

$$N = C_1{}^2 + C_2{}^2 + C_3{}^2 + \frac{2\sqrt{2}\,s}{\sqrt{1+s^2}}C_1(C_2+C_3) + 2s^2C_2C_3.$$

In general, C_j may be complex. However, for the sake of simplicity, Eq. 9 is written for the real values of C_j. If we allow C_1, C_2, and C_3 of Eq. 2 to take *any* real values, the maximum and minimum values which A_{12} can take are $1/(1+s)$ and $-1/(1-s)$ corresponding to the wave functions

$$\left.\begin{aligned}\Psi^{(\mathrm{B})} &= \frac{1}{\sqrt{2}}\frac{1}{1+s}\left\{\sqrt{1+s^2}\Phi_1 + \frac{1}{\sqrt{2}}(\Phi_2+\Phi_3)\right\}\\ \text{and}\qquad\qquad & \\ \Psi^{(\mathrm{AB})} &= \frac{1}{\sqrt{2}}\frac{1}{1-s}\left\{\sqrt{1+s^2}\Phi_1 - \frac{1}{\sqrt{2}}(\Phi_2+\Phi_3)\right\},\end{aligned}\right\} \tag{11}$$

respectively. Thus, we see that the most bonding state ($\Psi^{(\mathrm{B})}$) or the most antibonding state ($\Psi^{(\mathrm{AB})}$) is obtained in the case of *moderate* mixing of three configurations Φ_1, Φ_2, and Φ_3. This implies that admixture of the ionic configuration Φ_2 or Φ_3 with the covalent configuration Φ_1, or the delocalization of each odd electron to the other radical site, serves as an effective origin of bonding character between two weakly interacting radical sites. The importance of such electron delocalization in the bond formation between molecules or radicals was early pointed out.[16–19] In particular, special importance of a cross term arising from two configurations, corresponding in the present case to the terms of C_1C_2 or C_1C_3 in A_{12}, was stressed.[20–22]

The bonding character of a singlet biradical is thus represented by sA_{12}. In the light of the relation

$$A_{11} + 2sA_{12} + A_{22} = 2,$$

we can also measure the less bonding character by the quantity $1/2(A_{11}+A_{22})$.

Polar Character of Two Radical Sites

The density $\rho(1)$ also provides information as to what extent the two radical sites are polar. Evidently, polarity parallels $|A_{11}-A_{22}|$. We tentatively define the polar character of a singlet biradical by means of

$$\Pi = \left|\frac{A_{11}-A_{22}}{A_{11}+A_{22}}\right|, \tag{12}$$

in which

$$\left.\begin{aligned}A_{11} &= \frac{1}{N}\left(\frac{1}{1+s^2}C_1{}^2 + \frac{2\sqrt{2}\,s}{\sqrt{1+s^2}}C_1C_2 + 2C_2{}^2\right),\\ A_{22} &= \frac{1}{N}\left(\frac{1}{1+s^2}C_1{}^2 + \frac{2\sqrt{2}\,s}{\sqrt{1+s^2}}C_1C_3 + 2C_3{}^2\right).\end{aligned}\right\} \tag{13}$$

These are the coefficients of the $a(1)^2$ and $b(1)^2$ terms in $\rho(1)$ of Eq. 9 which is derived from a wave function Ψ already *correlation-extremized* according to the procedure in previous section.

By this definition, we have

$$\Pi(\Phi_1) = 0, \quad \Pi(\Phi_2) = \Pi(\Phi_3) = 1,$$

provided that Φ_1, Φ_2, and Φ_3 are correlation-extremized states.

A change in electron distribution can be expected to arise causing bonding stabilization through a moderate mixing of ionic structures. In this connection the work of Wulfman and Kumei,[23] who first pointed out the high possibility of polarization in singlet excited states of alkenes, is of interest.

Biradical Character of Singlet Biradicals

Since the bonding character between two radical sites becomes maximum only in the case of moderate admixing of ionic configurations with a covalent configuration, the less ionic character can not be adopted for the measure of biradical character.

We must take into account the following requisites which qualify a biradical:

1) The bonding character between two radical ends should be small since a species with too large bonding character might be called a molecule, but not a biradical. The value $1/2(A_{11}+A_{22})$ should not be small.

2) The polar character should not be large since a species with a strong inequality in electron density at the radical ends should be called a zwitterion. Namely, $(1-\Pi)$ should not be small.

A conventional but reasonable definition of the biradical character $\mathfrak{B}$ may therefore be given by

$$\begin{aligned}\mathfrak{B} &= \frac{1}{2}(A_{11}+A_{22})(1-\Pi) = \frac{1}{2}\{A_{11}+A_{22}-|A_{11}-A_{22}|\}\\ &= (\text{the smaller of } A_{11} \text{ and } A_{22}).\end{aligned} \tag{14}$$

Thus, the maximum possible biradical character in a *bonding* state is unity $(=1/(1+s))$, and the maximum biradical character in an *antibonding* state is larger than unity $(=1/(1-s))$. We also have

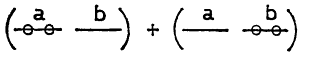
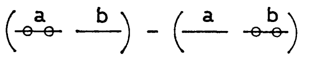
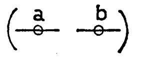
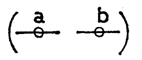
$$\mathfrak{B}(\Phi_1) = \frac{1}{1+s^2}, \quad \mathfrak{B}(\Phi_2) = 0, \quad \mathfrak{B}(\Phi_3) = 0,$$

in which Φ_1, Φ_2, and Φ_3 are the functions of Eq. 1, assuming that they are correlation-extremized ones.

The discussion can be easily extended to the case of complex wave functions.

Nonbonding Biradicals

It may happen that each odd electron occupies each of two orbitals orthogonal to each other so that the overlap integral s in Eq. 9 disappears. Hence, the

$\Psi^{(i)}$			γ	
$\frac{1}{\sqrt{2}}\{a(1)a(2)+b(1)b(2)\}$	$^1A_1$		$(aa\|aa)+(ab\|ab)$	≈ 0.89120 (a.u.)
$\frac{1}{\sqrt{2}}\{a(1)a(2)-b(1)b(2)\}$	$^1B_2$		$(aa\|aa)-(ab\|ab)$	≈ 0.88969
$\frac{1}{\sqrt{2}}\{a(1)b(2)+b(1)a(2)\}$	$^1B_1$		$(aa\|bb)+(ab\|ab)$	≈ 0.39420
$\left(\frac{1}{\sqrt{2}}\{a(1)b(2)-b(1)a(2)\}\right.$	$^3A_2$		$(aa\|bb)-(ab\|ab)$	$\left.\approx 0.39268\right)$

maximal biradical character is unity.

An example is perpendicular ethylene in which two orthogonal radical orbitals a and b are $(2p_x)_A$ and $(2p_y)_B$, respectively, A and B denoting two carbon atoms. In this case, it follows from symmetry relations that

$$\gamma_{12} = \gamma_{13} = 0, \quad S_{12} = S_{13} = 0$$

in Eq. 7. Thus, $\Phi_1 = 1/\sqrt{2}\{a(1)b(2)+b(1)a(2)\}$ is already a correlation-extremized wave function with which Φ_2 or Φ_3 of different symmetry does not mix. From the definition of Eq. 14, the state $\Psi^{(1)}=\Phi_1$ has the $\mathfrak{B}$ value of unity and can be called "purely" biradical. The other two states ($\Psi^{(2)}=1/\sqrt{2}(\Phi_2+\Phi_3)$ and $\Psi^{(3)}=1/\sqrt{2}(\Phi_2-\Phi_3)$) also have the $\mathfrak{B}$ value of unity. Such a biradical species may be called a *nonbonding biradical.*

The level situation of three correlation-extremized states is given above, together with the value of γ. The result is qualitatively consistent with that of numerical calculations.[24]

It is to be noted that the level gap between $^1B_1$ and $^3A_2$ states is very small (*ca.* 1 kcal/mol) in this example. The small S–T separation is characteristic of nonbonding biradicals. From an energetic point of view, they are expected to interchange easily between singlet and triplet states.

Biradical with Cyclic Orbitals

Singlet Oxygen. Let two ($^1\pi_g$) orbitals of the oxygen molecule be

$$\phi_x = \frac{1}{\sqrt{2-2s}}\{(2p_x)_1-(2p_x)_2\},$$

$$\phi_y = \frac{1}{\sqrt{2-2s}}\{(2p_y)_1-(2p_y)_2\},$$

where O_1-O_2 axis is parallel to the z-axis and s is the overlap integral of $(2p_x)_1$ and $(2p_x)_2$ or that of $(2p_y)_1$ and $(2p_y)_2$. Three configurations are specified by

$$\Phi_1 = \frac{1}{\sqrt{2}}\{\pi^+(1)\pi^-(2)+\pi^-(1)\pi^+(2)\},$$

$$\Phi_2 = \pi^+(1)\pi^+(2),$$

$$\Phi_3 = \pi^-(1)\pi^-(2),$$

where

$$\pi^+ = \frac{1}{\sqrt{2}}(\phi_x+i\phi_y),$$

$$\pi^- = \frac{1}{\sqrt{2}}(\phi_x-i\phi_y).$$

Φ_1, Φ_2, and Φ_3 of different symmetries are correlation-extremized wave functions corresponding to the stationary values of γ.

$$\Psi^{(i)} \qquad\qquad \gamma$$

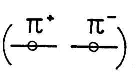
$$\Phi_1 = \frac{1}{\sqrt{2}}\{\phi_x(1)\phi_x(2)+\phi_y(1)\phi_y(2)\} \qquad {}^1\Sigma_g{}^+ \quad (xx|xx)+(xy|xy),$$

$$[\Phi_2, \Phi_3] = \left[\frac{1}{\sqrt{2}}\{\phi_x(1)\phi_x(2)-\phi_y(1)\phi_y(2)\},\ \frac{1}{\sqrt{2}}\{\phi_x(1)\phi_y(2)+\phi_y(1)\phi_x(2)\}\right] \qquad {}^1\Delta_g \quad \frac{1}{2}(xx|xx)+\frac{1}{2}(xx|yy),$$

$$\left(\frac{1}{\sqrt{2}}\{\phi_x(1)\phi_y(2)-\phi_y(1)\phi_x(2)\} \qquad {}^3\Sigma_g{}^- \quad (xx|yy)-(xy|xy)\right)$$

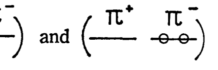
($(xy|xy)$, *etc.*, denote $(\phi_x\phi_y|\phi_x\phi_y)$, *etc.*).

The uppermost level corresponds to $^1\Sigma_g{}^+$ excited singlet state and the lower degenerate level to $^1\Delta_g$ state. The former stands for the configuration



with $\mathfrak{B}=1$. The species can thus be called purely biradical.

In the latter state, the correlation-extremized wave functions consist of purely doubly-occupied configurations



with $\mathfrak{B}=0$.

It should be noted that we have to employ the symmetry orbitals π^+ and π^- to construct wave functions with definite angular momenta.

Such cyclic orbitals, however, do not reflect the concept of radical site. The interpretation of $\mathfrak{B}$-values in this case should be made with certain reservation.

Cyclobutadiene (Planar Square). The orthogonal nonbonding orbitals can be taken as

$$\phi_1 = \frac{1}{\sqrt{2-2s'}}\{(2p_z)_4-(2p_z)_2\},$$

$$\phi_2 = \frac{1}{\sqrt{2-2s'}}\{(2p_z)_1-(2p_z)_3\},$$

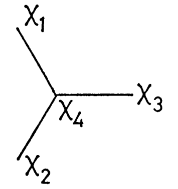
where $(2p_z)_j$ ($j=1$, 2, 3, and 4) are the four $2p_z$ orbitals and s' is the overlap integral of $(2p_z)_1$ and $(2p_z)_3$. The three states are as follows.

$$\begin{array}{lll} \Psi^{(i)} & & \gamma \\ \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_1(2)+\phi_2(1)\phi_2(2)\} & {}^1A_{1g} & (11|11)+(12|12), \\ \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_1(2)-\phi_2(1)\phi_2(2)\} & {}^1B_{1g} & (11|11)-(12|12), \\ \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_2(2)+\phi_2(1)\phi_1(2)\} & {}^1B_{2g} & (11|22)+(12|12), \\ \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_2(2)-\phi_2(1)\phi_1(2)\} & {}^3A_{2g} & (11|22)-(12|12), \end{array}$$

((11|22), *etc.*, denote $(\phi_1\phi_1|\phi_2\phi_2)$, *etc.*).

The level situation is consistent with the results of more elaborate calculations.[25)]

Singlet Planar Trimethylenemethane.[26)] The two orthogonal orbitals containing nonbonding electrons are written as



$$\phi_1 = \sqrt{\frac{2}{3(1-s')}}\left\{\chi_1 - \frac{1}{2}(\chi_2+\chi_3)\right\},$$

$$\phi_2 = \frac{1}{\sqrt{2(1-s')}}(\chi_2-\chi_3),$$

where χ_j ($j=1$, 2, 3, and 4) are the four $2p_z$ orbitals, and s' is the overlap integral of χ_1 and χ_2. The resulting three states are

$$\begin{array}{ll} {}^1A_1' & \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_1(2)+\phi_2(1)\phi_2(2)\}, \\ {}^1E' & \left\{\begin{array}{l} \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_2(2)+\phi_2(1)\phi_1(2)\}, \\ \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_1(2)-\phi_2(1)\phi_2(2)\}, \end{array}\right. \\ \left({}^3A_2' \right. & \left. \frac{1}{\sqrt{2}}\{\phi_1(1)\phi_2(2)-\phi_2(1)\phi_1(2)\} \right). \end{array}$$

The density of ${}^1E'$ ground state becomes

$$\rho(1) = \frac{2}{3(1-s')}[\{\chi_1(1)^2+\chi_2(1)^2+\chi_3(1)^2\} \\ -\{\chi_1(1)\chi_2(1)+\chi_1(1)\chi_3(1)+\chi_2(1)\chi_3(1)\}]$$

showing that this is an antibonding biradical with $\mathfrak{B}=1/(1-s')$. The antibonding character might primarily cause the nonpolar geometry of singlet ground-state trimethylenemethane.[27)]

General Characterization of Biradicals

The correlation-extremization approach developed in previous section is convenient for grasping a qualitative feature, but it can not be used in polar species where the potential field is partial to either one of the two radical sites. In such cases, the usual energy-extremization procedure, *viz.*, the configuration interaction (CI) approach, must be taken.

We use a CI wave function of n electron system $\Psi(1, 2, \cdots n)$ to construct the density distribution $\rho(1)$, which is decomposed in such a way as

$$\begin{aligned} \rho(1) = {} & A_{11}a(1)^2 + 2A_{12}a(1)b(1) + A_{22}b(1)^2 \\ & + 2\sum_j\{B_{aj}a(1) + B_{bj}b(1)\}\chi_j(1) \\ & + \sum_{j.k}B_{jk}\chi_j(1)\chi_k(1), \end{aligned} \tag{15}$$

The set of orbitals, a, b, and χ_j, in principle atomic hybrids or usual atomic orbitals, is obtained by a relevant transformation of the set of valence-shell atomic orbitals in such a way that orbitals a and b are appropriately associated with essentially located radical sites.

The bonding character and polar character can be represented by sA_{12} and Π of Eq. 12, respectively. We define a new concept, the delocalized character of a biradical, $\mathscr{D}$, by

$$\mathscr{D} = 2 - (A_{11}+2sA_{12}+A_{22}). \tag{16}$$

The biradical character of Eq. 14 can then be modified as

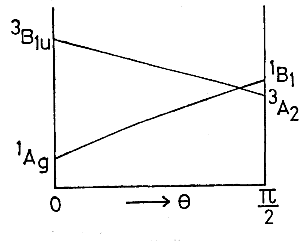
$$\begin{aligned} \mathfrak{B} & = \frac{A_{11}+A_{22}}{2-\mathscr{D}}(1-\Pi) \\ & = \frac{2}{2-\mathscr{D}}(\text{the smaller of } A_{11} \text{ and } A_{22}). \end{aligned} \tag{17}$$

Bonding Deformation of Singlet Biradicals

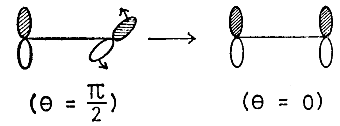
In the following examples, where the polar character Π can be put equal to zero, the biradical character $\mathfrak{B}$ depends only upon the overlapping between radical sites. Thus singlet biradicals stabilize with increasing overlapping between radical sites, which is in accordance with the direction of decreasing biradical character $\mathfrak{B}$. In contrast, the triplet species tend to decrease overlapping to stabilize.[29,30)]

A molecular deformation in singlet biradicals to raise overlapping may even take place when stabilization overcomes destabilization, if it arises, due to the deformation. It may happen that a triplet biradical with minimal overlapping shifts to the singlet state through intersystem crossing to cause stabilization by bonding deformation. Let us discuss the bonding deformation in the direction of decreasing $\mathfrak{B}$ with regard to several examples of singlet biradicals.

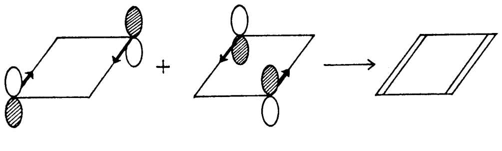
The dependence of energy on the torsional angle θ in perpendicular ethylene discussed in previous section is shown below.[24)] The lowest singlet has a deformation-instability in addition to the triplet-instability near $\theta=\pi/2$. The ${}^3A_2$ ground state of perpendicular geometry once formed may tend towards the planar form through the intersystem crossing to produce ${}^1A_g$ ground-state ethylene.



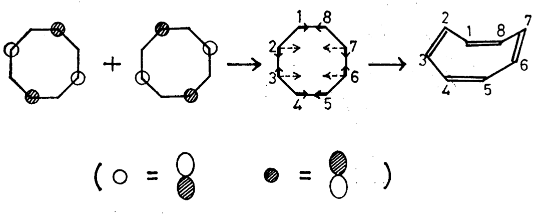
The direction of bonding deformation of perpendicular species is simply represented by the following orbital phase scheme.[28]



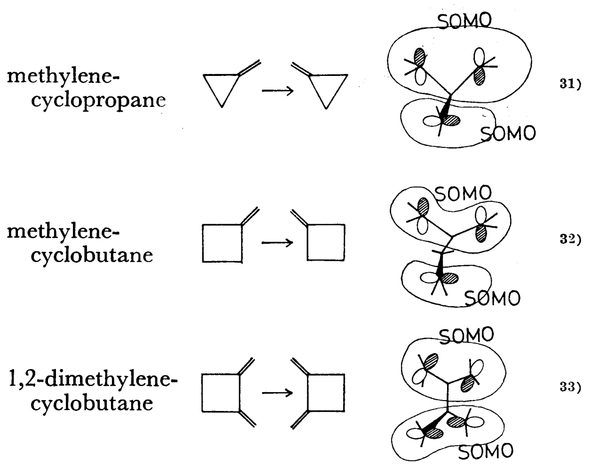
Similarly, the direction of deformation of square cyclobutadiene is given by the direction of in-phase overlapping of two odd-electron orbitals.



Also planar octagonal cyclooctatetraene will deform in the following way.

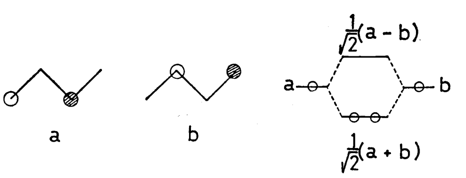


The bonding deformation consideration is employed to predict the geometry of stable intermediates in singlet radical reactions.

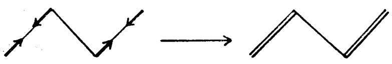


SOMO denotes a singly occupied molecular orbital.

The bond alternation in carbon $2p\pi$ chains can be explained by the following. The highest occupied (HO) and the lowest unoccupied (LU) MO's of a chain of equally distanced four p orbitals result approximately from the combination of the following two orbitals *a* and *b*.



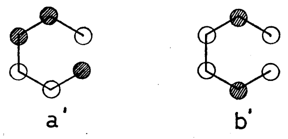
In this fictitious singlet biradical, the direction of deformation is also caused by the bonding overlapping of *a* and *b* to form a butadiene molecule, shown by



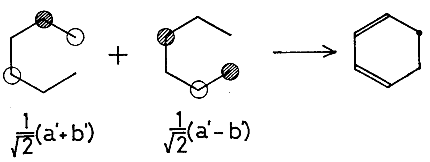
The lower occupied π orbital has hardly any connection with this deformation owing to its less nodal property.

Similarly, the difference in bond lengths in hexatriene, fulvene, naphthalene, *etc.*, is explained by considering the next HOMO's which contribute to the deformation less than HOMO because of their less nodal character.

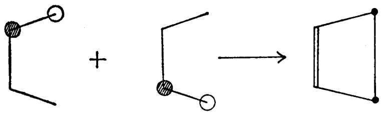
An interesting application of the bonding deformation approach may be the prediction of the reaction path in excited states. In the π-π^* excited singlet state of hexatriene, the highest half-occupied orbital (a') and the lowest unoccupied orbital (b') are represented by



In order to consider bonding stabilization of the electron in orbital a', let us construct in the place of a' and b' the following quasiorthogonal orbitals.



Combinations of these orbitals lead to orbitals a' and b', the former becoming occupied by a single electron to contribute to the bonding stabilization, and the direction of ring closure, if it occurs simultaneously, should be conrotatory. The conclusion is unchanged in the excited state with doubly occupied a'. In contrast, in the excited butadiene, the direction of hypothetical 1,4-bonding would be disrotatory.



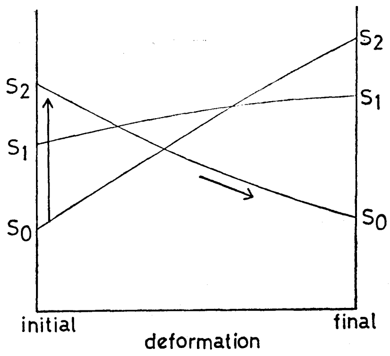
The lower singly occupied orbitals would contribute less by a similar discussion in terms of their less nodal property.

The simple approach is useful since it can be applied to a rough estimation of the direction of bonding in higher excited singlet states of a known electron configuration. The configuration might have several SOMO's. The general procedure is as follows:

i) By a linear combination of the HOMO (singly or doubly occupied) and the LUMO, say a' and b', we construct two MO's, *a* and *b*, which are mutually orthogonal and spatially separated from each other to construct a fictitious singlet biradical species.

ii) The direction of maximal overlapping of *a* and *b* to decrease the biradical character $\mathfrak{B}$, obtained by the usual procedure in the orbital interaction approach,[28] leads to a favourable reaction path.

In some cases, an excited state of the species before deformation may correlate to the ground state of the species after deformation, as in the following,

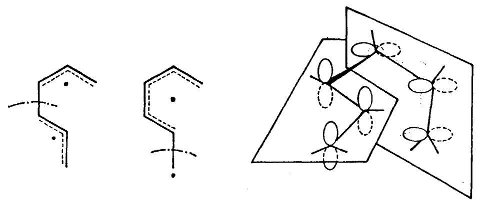


An example is the hypothetical disrotatory cyclization of S_2 excited butadiene to S_0 cyclobutene in the Longuet-Higgins-Abrahamson state correlation diagram.[34] The direction of such processes can be discussed by the method mentioned above.

Unpaired-Electron Isolating Deformation or Bonding in Triplet Biradicals

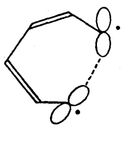
Once a triplet state is formed photochemically or thermally, a deformation or bond formation may be liable to take place to acquire stabilization in such a way that each of the two unpaired-electrons enters each of two orthogonal orbitals, or they become separated from each other by the newly formed bond as far away as possible.[9,30] In this connection Michl's conception of "loose" and "tight" biradicaloids is useful.[30c] The following examples are given for illustration.

Consider a π-π^* triplet hexatriene molecule. Twisting of the carbon chain would certainly diminish the overlapping of the two unpaired-electron orbitals. Two possibilities exist in regard to the twisting.

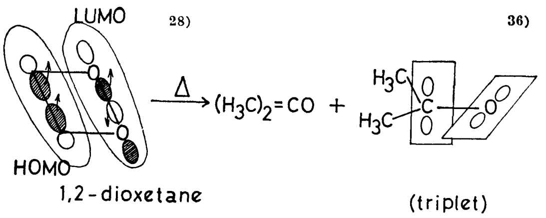


(I) (II) (III)

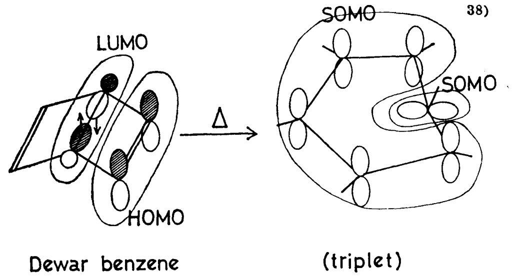
The sum of conjugation stabilization in the two separated parts in (I) is greater than in (II). The resulting geometry is shown in (III). Courtot and Salaün[35a] showed that sensitized photoreactions of hexatrienes preferentially cause the *cis-trans* isomerization of the *central* double bond, and that the singlet reaction causes isomerization of the terminal double bonds. The results are consistent with the theoretical prediction by Baird and West[35b] that the twisting of inner bonds should be preferred in the lowest triplet excited state of polyenes. In the singlet reaction a structure essentially like may be prevalent on account of the bonding nature of singlet biradicals, which will favour the terminal bond isomerization.

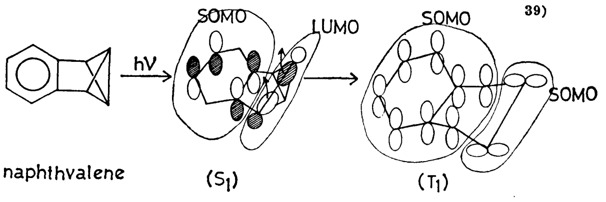


Geometries in which the planes associated with two unpaired-electron orbitals are perpendicular to each other might be expected more widely.[35c]

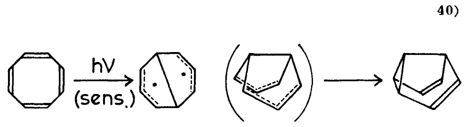


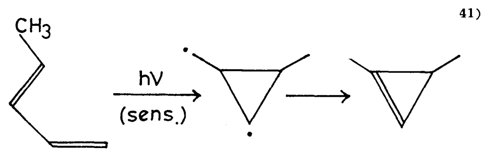
(Similar reactions are considered in chemiluminescent decomposition of 1,2-dioxetanone derivatives.[37])



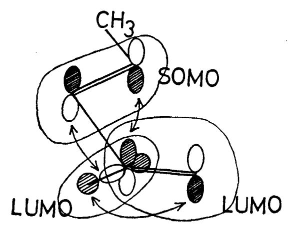


The above are examples of the separation of unpaired-electron orbitals by deformation. The isolation of unpaired-electrons also takes place by the formation of separating bonds.





In the singlet-state reaction, a similar reaction takes place. In this case a certain concertedness may be mixed in the mechanism.[28]



It appears that combination of the principle of unpaired-electron isolation in the triplet state with that of bonding deformation in the singlet state brings about a plausible mechanism occasionally prevalent in photochemical processes in which biradicaloid intermediates play an important role.

Suppose that the lowest triplet state (T_1) is produced, in some cases from higher excited singlet states (S_n) *via* S_1, through radiationless transitions (triplet biradical formation by a nonsensitized photoprocess). A possible deformation path might be composed of stages (I) and (II) as shown in Fig. 1.

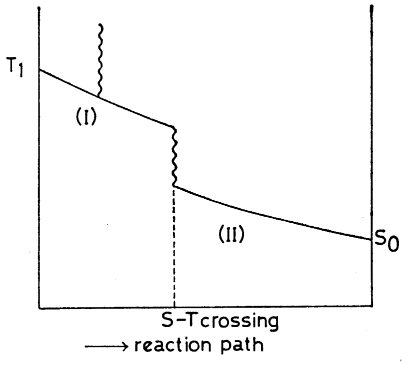


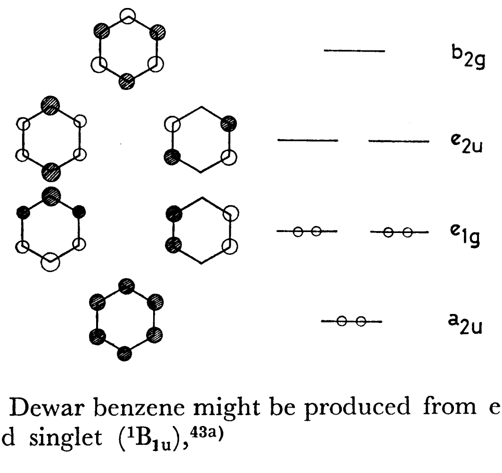
Fig. 1. A possible reaction path. (S_0: singlet ground state; T_1: first triplet state; 〰〰: radiationless transition)

Stage (I) involves separation of unpaired-electron orbitals by orthogonally twisting deformation or bond formation, occuring in the first triplet state. Stage (II) is that of bonding deformation or bond formation in the singlet ground state, S_0.

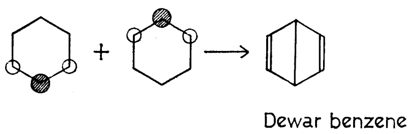
By considering intermediate T_1, stereoselective phenomena can be explained by the augmenting chance to undergo further conversion due to the long lifetime of the triplet state.

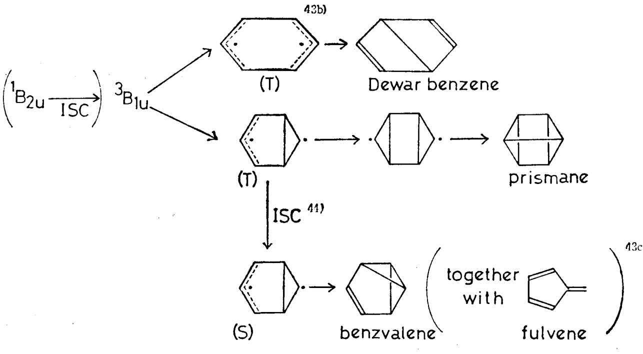
This mechanism of the intermediation of triplet state is supported by Kushick and Rice[42] as regards the effectuation of the S-T transition by dynamical coupling of the torsional motion around the C_1–C_2 bond in the *cis-trans* photoisomerization of butadiene.

Let us consider excited-state reactions of benzene, six π MO's of which are given below.



Thus, Dewar benzene might be produced from $e_{1g} \rightarrow e_{2u}$ excited singlet ($^1B_{1u}$),[43a) and the formation of benzvalene, prismane, and Dewar benzene would be favoured by triplet intermediation.





The mechanism involved might control the direction of reaction, giving a new principle of orientation or stereoselection in excited-state reactions.

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