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Photochemical Dimerization of *p*-Benzoquinone Methyl Derivatives in Crystals

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Photochemical dimerization of *p*-benzoquinone and its methyl derivatives in crystals is discussed assuming that the reactivity is parallel with the stabilization energy of the transient complex. The calculation is carried out by taking both the terms of electronic structure of the monomer molecule and the intermolecular arrangement in the monomer crystal into consideration. Concerning the ability of photodimerization, the result obtained is qualitatively satisfactory. However, such an agreement with experiment cannot be obtained if either the electronic term or the geometrical term is ignored.

Die photochemische Dimerisierung von *p*-Benzochinon und seines Methylderivates im Kristallzustand wird diskutiert; dabei wird angenommen, daß die Reaktivität parallel zur Stabilisierungsenergie des Übergangskomplexes ist. Die Berechnung wird so durchgeführt, daß sowohl die Elektronenstruktur des monomeren Moleküls als auch die Lage der Moleküle im Kristall des Monomeren berücksichtigt wird. Die Ergebnisse bezüglich der Fähigkeit zur Photodimerisierung sind qualitativ zufriedenstellend. Eine derartige Übereinstimmung mit dem Experiment kann jedoch nicht erhalten werden, wenn entweder der elektronische Beitrag oder der geometrische Beitrag vernachlässigt werden.

La dimérisation photochimique de la *p*-benzoquinone et de ses dérivés méthylés dans les cristaux est discutée en supposant que la réactivité évolue parallèlement à l'énergie de stabilisation du complexe de transition. Le calcul est effectué en tenant compte de la structure électronique du monomère et de l'arrangement intermoléculaire dans le cristal du monomère. Le résultat obtenu est satisfaisant qualitativement en ce qui concerne la facilité de photodimérisation. Cependant, un tel accord avec l'expérience ne pourrait être obtenu si l'un des deux termes électronique ou géométrique était négligé.

Introduction

On the photochemical reaction in crystals, the electronic structure of the molecules and their arrangements in the unit cell are two of the most dominant characters for discussing the reactivity. Recently, Rabinovich and Schmidt [1] investigated the photodimerization of the *p*-benzoquinone methyl derivatives and other systems with double bonds in connection with the relation between the reactivity and the packing geometry. As a result, they postulated that the photodimerization occurs only when the monomer crystal contains the nearest neighbouring molecules with parallel double bonds. On the other hand, Fukui, Morokuma and Yonezawa [2] discussed the photochemical reaction in terms of the molecular orbitals by assuming the reactivity to be proportional with the π-stabilization energy in the transition state. Nagata *et al.* [3] applied this treatment to some aromatic molecules and obtained the distinct parallelism between the π-delocalization energy and the degrees of dimer-forming ability. However, these two works were not clearly concerned with the intermolecular arrangement in the crystal, because their main purpose was not the solid-state reaction. Although there were several other theoretical investigations on the photochemical reaction [4], most of them were carried out with reference to the excited state or the transition state by taking only the change of electronic structure in the isolated group of reactant into consideration. Under these circumstances, it may be said that most of theoretical works on photochemical reaction have not completely be satisfactory to the process in crystals.

In the present paper, the photochemical dimerization of *p*-benzoquinone and its methyl derivatives in crystals by near-ultraviolet irradiation [5] will be discussed taking both the terms of electronic structure of the monomer molecule and the intermolecular arrangement in the monomer crystal into consideration. In this case, a following simplified process was assumed, that is, a photo-excited molecule M* reacts with an unexcited molecule M and forms a stable photodimer M−M through a transient complex ((M---M)* as follows:

$$M^* + M \longrightarrow (M{-}{-}{-}M)^* \longrightarrow M{-}M\,. \tag{1}$$

In some cases, such a complex may behave as an exciton which moves among the corresponding sites by a jumping process assisted by phonon and forms a stable photodimer by being trapped at some defect. However, such a process is not always greatly important for discussing the ability of photodimerization, but the stability of the transient complex which is capable of coupling with phonon is a predominant factor as will be shown in the following sections.

Method and Calculation

In the present work, the ability of the photodimerization is assumed to be parallel with the stabilization energy of the transient complex, that is, the energy difference between the systems A + A* and (A---A)*, as in the work by Fukui *et al.* [2]. The simple LCAO-MO approximation was adopted here. If the photodimerization initiates by the excitation of an electron from one of the occupied orbitals ϕ_M^O to one of the vacant orbitals ϕ_M^V of the concerned molecule M, the wavefunction of the transient complex may simply be constructed from the following four zero-order functions[1]:

$$\phi_1 = \mathscr{A}\,\phi_A^O(1)\,\phi_A^V(2)\,\phi_B^O(3)\,\phi_B^O(4)\,, \tag{2}$$

$$\phi_2 = \mathscr{A}\,\phi_A^O(1)\,\phi_B^V(2)\,\phi_B^O(3)\,\phi_B^O(4)\,, \tag{3}$$

$$\phi_3 = \mathscr{A}\,\phi_A^O(1)\,\phi_A^O(2)\,\phi_A^V(3)\,\phi_B^O(4)\,, \tag{4}$$

$$\phi_4 = \mathscr{A}\,\phi_A^O(1)\,\phi_A^O(2)\,\phi_B^V(3)\,\phi_B^O(4)\,, \tag{5}$$

where $\mathscr{A}$ is an operator of antisymmetrization and normalization, and the non-orthogonality between orbitals of the different atoms is disregarded. The secular

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[1] In the treatment of Fukui *et al.* [2] and the calculation by Nagata *et al.* [3], the wavefunction of ϕ_4 and the energy difference of the charge transfer states [ϕ_2 and ϕ_3] from the homopolar states [ϕ_1 and ϕ_4] were disregarded.

determinant obtained from these functions is as follows:

$$\begin{vmatrix} E_0-E & W_V & -W_O & 0 \\ W_V & E^*-E & 0 & -W_O \\ -W_O & 0 & E^*-E & W_V \\ 0 & -W_O & W_V & E_0-E \end{vmatrix} = 0\,. \tag{6}$$

Here, E_0 is the sum of the energies of the excited and the unexcited monomers, and E^* is the energy of a pair of charge-transfered monomers, while W_O and W_V are given by

$$W_O = \int \phi_A^{O*} H \phi_B^O \, d\tau \tag{7}$$

and

$$W_V = \int \phi_A^{V*} H \phi_B^V \, d\tau \tag{8}$$

(H is the one-electron Hamiltonian of the system). As a result, the energy of the transient complex is easily obtained as

$$E = \tfrac{1}{2}(E_0 + E^*) \pm [\tfrac{1}{4}(E_0 - E^*)^2 + (W_O \pm W_V)^2]^{1/2}\,. \tag{9}$$

In actual, the resonance integrals, W_O and W_V, were assumed to be proportional to the intermolecular overlap integrals between the corresponding orbitals. That is

$$W_O \simeq \kappa S_{AB}^O = \kappa \int \phi_A^{O*} \phi_B^O \, d\tau = \kappa \sum_i \sum_j c_{iA}^O c_{jB}^O S_{iAjB} \tag{10}$$

and

$$W_V \simeq \kappa S_{AB}^V = \kappa \int \phi_A^{V*} \phi_B^V \, d\tau = \kappa \sum_i \sum_j c_{iA}^V c_{jB}^V S_{iAjB}\,, \tag{11}$$

where κ is a proportional constant, c_{iM}^O and c_{iM}^V are the coefficients of the ith atomic orbital in the ϕ_M^O and the ϕ_M^V orbitals, respectively, and S_{iAjB} is the overlap integral between the ith atomic orbital of molecule A and the jth atomic orbital of molecule B. Since in the bracket of Eq. (9) the first term is much larger than the last term, the stabilization energy of transient complex which corresponds to the lowest energy state resulting from the above interaction may be expressed as follows:

$$\Delta E \simeq \frac{(|W_O| + |W_V|)^2}{E^* - E_0} \tag{12}$$

$$\simeq \frac{\kappa^2}{E^* - E_0}(|S_{AB}^O| + |S_{AB}^V|)^2\,. \tag{13}$$

Actually, there are various kinds of pairs of molecules in crystals, and the overlap integrals are different according to the relative intermolecular arrangement. Hereafter, the molecules will be distinguished by using symbols, A_{pqr}, $\bar{A}_{pqr}$, B_{pqr}, and $\bar{B}_{pqr}$, according to the orientations in the crystal, and their meanings are summarized in the footnotes of Table 1.

The molecular orbitals of the monomers used were the simple LCAO-MO's with the parameters by Streitwieser [6]. In this case, the conjugation model was used for the methyl group. The intermolecular overlap integrals were calculated by using the self-consistent field atomic orbitals (SCF-AO's) of the ground state of carbon (^3P) and oxygen (^3P) by Clementi [7] and the pseud-p orbitals

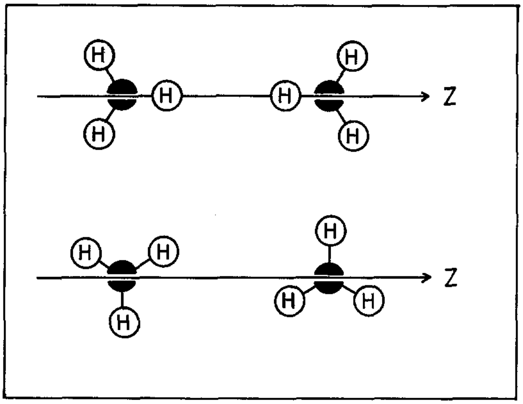

Fig. 1. Four typical configurations of the H_3 group

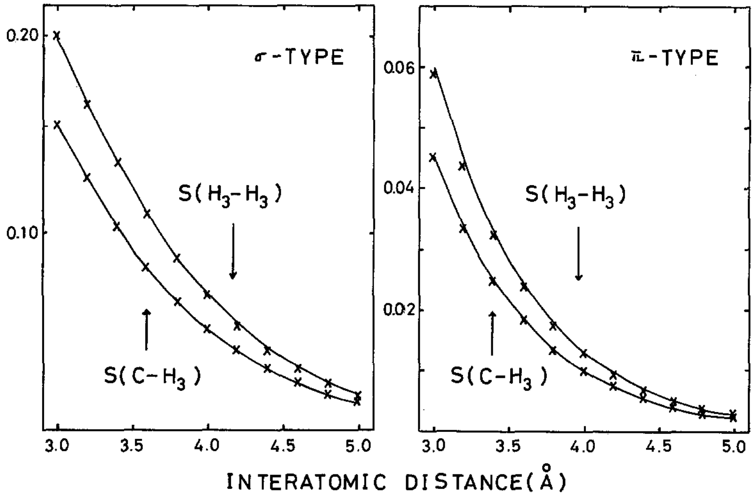

Fig. 2. The relations among the mean value of the exact overlap integrals (solid line) and that of the overlaps using the approximate pseud-*p* H_3 orbitals with $\delta = 1.17$ (×)

of H_3 group. In the present work, the pseud-*p* orbital was approximated as a single term of Slater-type 2*p* orbital centered on the center of gravity of the H_3 group[2]. Its orbital exponent of δ was chosen to be 1.17 so as to give the mean value of the exact overlap integrals between the carbon 2*p* and the pseud-*p* orbitals and those between the two pseud-*p* orbitals among the cases of each four typical configurations of the H_3 group shown in Fig. 1, at the center-to-center distances of 3.0 Å to 5.0 Å. Here, the exact overlap integral means the overlap integral which was calculated by using the pseud-*p* orbital constructed from the three hydrogen 1*s* orbitals with orbital exponent of 1.00, instead of the Slater-type 2*p* orbital. Fig. 2 shows the relations among the mean value of the exact overlap integrals

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[2] This approximation makes the formulation feasible to be easier than that in the use of the pseud-*p* orbital constructed from three hydrogen 1*s* orbitals.

and the value of overlap integrals using the approximate pseud-p H_3 orbitals with $\delta = 1.17$.

As the photodimerization of p-benzoquinone (PBQ) methyl derivatives occurs by near-ultraviolet irradiation, the reaction is considered to be initiated by one of the following transitions [8]:

[I] Forbidden $n - \pi^*$ transition near 4300 Å from the nonbonding orbitals which are mainly localized at two oxygen atoms to the lowest vacant π orbital ($b_{2g} \leftarrow b_{2u}$ and $b_{2g} \leftarrow b_{3g}$ for PBQ[3]).

[II] Forbidden $\pi - \pi^*$ transition near 3000 Å from the highest occupied π orbital to the lowest vacant π orbital ($b_{2g} \leftarrow b_{1g}$ for PBQ[3]).

[III] Allowed $\pi - \pi^*$ transition near 2500 Å from the second highest occupied π orbital to the lowest vacant π orbital ($b_{2g} \leftarrow b_{3u}$ for PBQ[3]).

The transitions of [I] and [II] cannot always be forbidden from only the consideration of symmetry except for the PBQ and the tetramethyl p-benzoquinone (TMPBQ) (duroquinone) molecule with symmetry of D_{2h}. For convenience, however, the above classification will be used for all the molecules treated here.

It may be noted that the simple LCAO-MO calculation of PBQ with Streitwieser's parameters gives the reversed order against the experimental result, that is, the representation of the highest and the second highest occupied π orbital are b_{3u} and b_{1g}, respectively. In the present work, therefore, these orbitals were chosen so as to be consistent with the experimental result. Although the delocalization from the two oxygen atoms should be taken into account for the detailed calculation, the nonbonding orbitals used were simply be approximated as $2^{-1/2}(p_O \pm p_{O'})$ where the p_O and $p_{O'}$ are the $2p$ orbitals of each oxygen atom and perpendicular to the line with the two oxygen atoms in the molecular plane.

In the present work, all the carbon and oxygen atoms in each monomer were assumed to be located in a plane, since only very small deviations of such heavy atoms were found from the conventional best plane. The calculation was performed by choosing to take any pair of molecules with the constituent atom which is not less than 6.0 Å apart[4]. In Table 1, the values $(|S^O_{AB}| + |S^V_{AB}|)^2$ are given as a measure of the stabilization energies (13), together with the space groups of the monomer crystals.

For reference, the stabilization energy of transient complex ΔE (12) was also calculated by disregarding the effect of intermolecular arrangement in crystals as in the treatment by Fukui *et al.* [2]. In this case, W_O and W_V were assumed to be proportional to the resonance integral between the atomic orbitals concerned with the dimer formation, that is,

$$W_O \simeq \gamma(c^O_{pA} c^O_{rB} + c^O_{qA} c^O_{sB}) \tag{14}$$

and

$$W_V \simeq \gamma(c^V_{pA} c^V_{rB} + c^V_{qA} c^V_{sB}), \tag{15}$$

where γ is the resonance integral between the π orbitals concerned with the formation of bonds, $p_A - r_B$ and $q_A - s_B$ (p, q, and r, s are the reaction centers of monomer, A and B, respectively). The results so obtained are given in Table 2.

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[3] Mulliken's notation [9] was used.

[4] The packing arrangements of the molecules in the crystals were taken from the data given in papers cited in Ref. [10].

Discussion

In the present work, all the molecules treated are the *p*-benzoquinone and its methyl derivatives, and their electronic properties are fairly similar to each other. In all the excited states in question, the energy difference between the homopolar and the charge-transfered configurations in the transient complex, $E^* - E_0$, may correspond to that between the ionization potential from the highest singly occupied π orbital of the excited state (the lowest vacant π orbital in the ground state) and the electron affinity to the same orbital of the molecule. As a result, the value of $(E^* - E_0)$ is not much different according to the four kinds of the transient states in all the molecules in question. Adopting the relation of Eq. (13), therefore, one may approximately be possible to use $(|S^O_{AB}| + |S^V_{AB}|)^2$ as a measure of the stabilization energy of the transient complex.

As can be seen in Table 1, the value of $(|S^O_{AB}| + |S^V_{AB}|)^2$ is different according to the excited states concerned, because the intermolecular overlap integrals are much dependent on the form of the molecular orbital. In general, it is certainly large for the transient complex produced by the forbidden $\pi - \pi^*$ transition [II] as compared with the other states except for the TMPBQ. It may be noted here that *the largest value of the stabilization energies for each dimer-forming molecule* [2,3-, 2,5-, and 2,6-dimethyl *p*-benzoquinone (DMPBQ)] *is considerably larger than that of the molecules which have not yet been detected the stable photodimers* [PBQ and TMPBQ]. That is, the former values are about five times and twice as large as that of the PBQ (transition [II]) and the TMPBQ (transition [III]), respectively.

In reference to the fact that the above value of the TMPBQ is not very small, one may keep the following points in mind. As is described above, the reactive transient complex may be produced by the allowed $\pi - \pi^*$ transition only for the TMPBQ. The light needed for the excitation may not effectively be irradiated on the crystal, since the experiment [5] was carried out at room temperature by irradiating these molecules through Pyrex glass with a 125-w medium-pressure mercury arc or with sunlight. Furthermore, the fact that the TMPBQ does yield the stable photopolymers without photodimers comes into question. In the most of the crystals treated here, there are not more than two adjacent molecules with the largest value of $(|S^O_{AB}| + |S^V_{AB}|)^2$. Only for the TMPBQ crystal, however, there are such four neighbours and the group of these molecules constitutes a two-dimensional reticulum being composed of four-membered rings. As a result, they may possibly tend to yield the photopolymers without terminating at the dimer-formation by the ultraviolet irradiation as compared with the one-dimensional case.

In fact, the simple representation of Eq. (13) may actually be useful in predicting the dimer-forming ability, although it does not strictly express the stabilization energy of the transient complex. Apparently, the present treatment includes several approximations and assumptions. The use of the $2p$-type H_3 orbital arouses some error in the overlap integrals because such an orbital gives only the mean value among the typical intermolecular configurations of the H_3 group but not the value corresponding to each orientation, although the difference between them is rather small. However, the present selection may possibly be adequate

Table 1. π *stabilization energy* ΔE *(in unit of* $\{\kappa^2/[E^* - E_0]\} \times 10^{-6}$*)*: $[\{|S^{O}_{AB}| + |S^{V}_{AB}|\}^2 \times 10^6]$

Substance	*p*-benzoquinone[a]		2,3-dimethyl[a] *p*-benzoquinone		2,5-dimethyl[b] *p*-benzoquinone		2,6-dimethyl[a] *p*-benzoquinone		tetramethyl[b] *p*-benzoquinone	
Space group	$P2_1/a$		$P2_1/a$		$P\bar{1}$		$P2_1/a$		$P\bar{1}$	
Reactivity	−		+		+		+		−	
Transition [I+][c]	$A_{000}-A_{010}$	23	$A_{000}-\bar{A}_{000}$	155	$B_{000}-B_{100}$	325	$A_{000}-A_{010}$	161	$A_{000}-B_{000}$	2
	$-A_{001}$	9	$-\bar{A}_{001}$	68	$-A_{100}$	2	$-\bar{A}_{101}$	4	$B_{000}-A_{100}$	2
	$-B_{000}$	2	$-\bar{A}_{101}$	15	$-A_{001}$	2	$-\bar{A}_{111}$	4		
					$-A_{110}$	2	$-\bar{A}_{100}$	1		
Transition [I−][c]	$A_{000}-A_{010}$	23	$A_{000}-\bar{A}_{000}$	154	$B_{000}-B_{100}$	315	$A_{000}-A_{010}$	157	$A_{000}-B_{000}$	5
	$-A_{001}$	7	$-\bar{A}_{001}$	68	$-A_{100}$	2	$-\bar{A}_{111}$	3	$B_{000}-A_{100}$	5
	$-B_{000}$	3	$-\bar{A}_{101}$	14	$-A_{001}$	2	$-\bar{A}_{101}$	3		
					$-A_{110}$	2	$-\bar{A}_{100}$	1		
Transition [II]	$A_{000}-B_{000}$	339	$A_{000}-\bar{A}_{000}$	1474	$B_{000}-B_{100}$	2169	$A_{000}-A_{010}$	1771	$B_{000}-A_{100}$	22
	$-A_{001}$	200	$-\bar{A}_{001}$	888	$A_{000}-A_{100}$	245	$-\bar{A}_{101}$	106	$A_{000}-B_{000}$	21
	$-B_{001}$	3	$-\bar{B}_{000}$	3	$B_{000}-A_{010}$	3	$-\bar{A}_{111}$	2		
	$-A_{010}$	2	$-\bar{A}_{\bar{1}00}$	3	$-A_{101}$	3				
			$-\bar{A}_{101}$	1	$-B_{010}$	3				
					$A_{000}-A_{010}$	2				
					$B_{000}-A_{110}$	1				
					$-A_{001}$	1				
Transition [III]	$A_{000}-A_{001}$	12	$A_{000}-\bar{A}_{000}$	196	$B_{000}-B_{100}$	287	$A_{000}-A_{010}$	277	$B_{000}-A_{100}$	811
	$-A_{010}$	7	$-\bar{A}_{001}$	69	$A_{000}-A_{100}$	149	$-\bar{A}_{101}$	14	$A_{000}-B_{000}$	809
	$-B_{000}$	6	$-\bar{A}_{101}$	5	$-B_{000}$	5	$-\bar{A}_{100}$	4		
	$-B_{001}$	4	$-\bar{B}_{0\bar{1}0}$	4	$B_{000}-A_{100}$	2	$-\bar{A}_{111}$	1		
					$-A_{001}$	2				
					$-A_{110}$	2				

[a] Co-ordinates of equivalent positions — Symbol

x,	y,	z,	A
$-x$,	$-y$,	$-z$,	$\bar{A}$
$-x$,	$(1/2)+y$,	$(1/2)-z$,	B
x,	$(1/2)-y$,	$(1/2)+z$,	$\bar{B}$.

[b] Co-ordinates of equivalent positions — Symbol

x,	y,	z,	A
x',	y',	z',	B

A_{pqr} denotes fractional co-ordinates $p+x$, $q+y$, $r+z$.

[c] The values for Transitions [I±] were calculated using the nonbonding orbital of $2^{-1/2}(p_O \pm p_{O'})$, respectively.

because of some uncertainty of position of protons in the data of X-ray diffraction. Concerning the simplified nonbonding orbitals, only the minor influence is expected because of the very small intermolecular overlap integrals concerned. For the 2,3-DMPBQ molecule, the mixing of the two configurations excited from the highest and the second highest π orbitals to the lowest vacant π orbital should be taken into account for the precise discussion, because the calculated transition moments from the ground state to these two configurations are nearly the same in the approximation without configuration interaction in spite of the much different experimental values [8]. Further, there are other electronic excited

Table 2. *Maximum π stabilization energy* ΔE *(in unit of* $\gamma^2/[E^* - E_0]$*)*: $(\{|c_p^O c_q^O + c_r^O c_s^O| + |c_p^V c_q^V + c_r^V c_s^V|\}^2)$

Substance	*p*-benzoquinone	2,3-dimethyl *p*-benzoquinone	2,5-dimethyl *p*-benzoquinone	2,6-dimethyl *p*-benzoquinone	tetramethyl *p*-benzoquinone
Reactivity	−	+	+	+	−
Transition [I ±][a]	0.053	0.057	0.051	0.054	0.049
Transition [II]	0.428	0.581	0.382	0.384	0.346
Transition [III]	0.165	0.605	0.159	0.162	0.143

[a] The values for Transitions [I ±] were calculated using the nonbonding orbital of $2^{-1/2}(p_O \pm p_{O'})$, respectively.

configurations which were disregarded in calculating the energy of transient complex. However, these points may not substantially be important for obtaining a static index of ability of photodimerization in crystals, although they have influence on only minor numerical values in the final result.

In the calculation disregarding the effect of the packing arrangement, no parallelism was obtained between the ability of photodimerization and the stabilization energy of the transient complex. That is, the stabilization energies obtained for the dimer-forming molecules of 2,5- and 2,6-DMPBQ are certainly smaller than that of the PBQ which was not detected the stable photodimers. This means that the ignorance of packing arrangement is quite inadequate in discussing the photochemical reaction in crystals, even in a qualitative sense. By the way, the treatment disregarding the energy difference between the homopolar and the charge-transfered configuration in the transient complex is qualitatively parallel with the above calculation except that the stabilization energy is proportional to $|W_O| + |W_V|$ but not its square.

In the PBQ crystal, the nearest neighbouring molecule of A_{000} is B_{000}, while the stabilization energies of ΔE $(A_{000} - B_{000})$ are rather small as compared with $\Delta E\,(A_{000} - A_{001})$ or $\Delta E\,(A_{000} - A_{010})$ except for the forbidden $\pi - \pi^*$ transition [II]. This is certainly due to the fact that the molecular plane of B_{000} is not parallel to that of A_{000} because the latter is transformed into the former after the screw translation. On the other hand, the largest stabilization energies are actually very large for all the transient complexes of the 2,3-, 2,5-, and 2,6-DMPBQ treated here, since all the nearest neighbouring molecules in pairs are parallel each other, that is, $A_{000} - \bar{A}_{000}$ for 2,3-DMPBQ, $B_{000} - B_{100}$ for 2,5-DMPBQ, and $A_{000} - A_{010}$ for 2,6-DMPBQ. On the contrary, a large stabilization energy cannot be obtained from the nearest neighbouring molecules of TMPBQ, since B_{000} and A_{100}, or A_{000} and B_{000}, are not parallel to each other.

In view of these facts, the stabilization energy ΔE is generally large if the sum of the absolute values of intermolecular overlap integrals, S_{AB}^O and S_{AB}^V, is large, or if the signs of the coefficients of atomic orbitals concerned with the large intermolecular overlap integrals are almost the same in the same LCAO-MO's $[\phi_M^O$ and ϕ_M^V (M = A or B)] of the different molecules. Such a condition may often be satisfied when the molecules in a pair are transformed each other by the primitive translational operation along the normal of the molecular plane. Accordingly, Schmidt's expression that there are the nearest neighbouring molecules with "parallel double bond" is apparently ambiguous and not the satisfactory condition for determing the ability of photodimerization.

Although the present work uses a rather simplified treatment and the comparable experimental data are not always completely sufficient, the results obtained are qualitatively satisfactory for discussing the photodimerization of *p*-benzoquinone methyl derivatives. The use of $(|S^O_{AB}| + |S^V_{AB}|)^2$ as a measure of the stabilization energy is valid when comparing the molecular crystals with close energy difference between the homopolar and the charge-transfered configurations in the transient complex. Accordingly, a quantitative comparison between the calculated value and the experimental result may greatly be of interest for a system where the quantum yield has been obtained according to the various wavelengths used. As a further problem, the influence of the lattice vibration should be included in a more detailed discussion.

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