Photoinduced ω -bond dissociation of *m*-halomethylbenzophenones studied by laser photolysis techniques and DFT calculations. Substituted position effects[†]

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Photochemical profiles of ω -cleavage of carbon–X (X = Br and Cl) bonds in *m*-bromo- and *m*-chloromethylbenzophenones (*m*-BMBP and *m*-CMBP) were investigated by laser photolysis techniques and DFT calculations. *m*-BMBP and *m*-CMBP were found to undergo ω -bond cleavage to yield the *m*-benzoylbenzyl radical (*m*-BBR) at 295 K, and the quantum yields were determined. No CIDEP signal was detected upon 308 nm laser photolysis of both the compounds. From these observations, it was inferred that the ω -bond of these *m*-halomethylbenzophenones (*m*-HMBP) cleaves in the lowest excited singlet state (S₁(n, π^*)) upon direct excitation. Upon triplet sensitization of acetone (Ac), the *m*-BBR formation was observed in transient absorption for an Ac–*m*-BMBP was determined. In contrast, formation of triplet *m*-CMBP was seen for an Ac–*m*-CMBP system. Absence of C–Cl bond cleavage in the triplet state of *m*-CMBP indicated the reactive state of *m*-CMBP for ω -cleavage is only the S₁(n, π^*) state. Based on the efficiencies and DFT calculations for excited state energies, photoinduced ω -bond dissociation of *m*- and *p*-HMBPs was characterized.

1. Introduction

Photoinduced bond cleavage is one of the well-known reactions in photochemistry and photobiology. As with photochemical reactions of carbonyl compounds, Norrish type I and II reactions where carbon–carbon bond fission occurs at the α and β -positions of the carbonyl, respectively, have been widely documented by means of product analysis and time-resolved transient measurements as well as carbon-heteroatom dissociation occurring at the α - and β -positions of aromatic carbonyls.¹⁻²⁸ Less attention, however, has been paid to photoinduced rupture of remote carbon-heteroatom bonds in aromatic carbonyl compounds, that is at positions other than the α - or β -position of the carbonyl.²⁹⁻³⁵ Recently, we also have been studying photolytic bond cleavage which occurs neither at α - nor β -position, but namely, at the ω -position of benzophenone (BP) and naphthyl phenyl ketone (NPK) derivatives by using time-resolved EPR and laser photolysis techniques.36-40 w-Cleavage of C-S, C-Cl and C-Br bonds has been characterized to occur mainly in the lowest triplet (T_1) state. It seems that for occurrence of ω -bond dissociation, the enthalpy of the cleaving bond must be smaller than the triplet energy. Indeed the bond enthalpies for the cleavable C-Cl, C-S and C-Br bonds in the BP and NPK derivatives were smaller than the corresponding triplet energies^{36,37,39,40} while BP derivatives having an enthalpy for the C-O or C-Si bonding larger than the triplet energies was inert to photodecomposition.^{35a,39} Interestingly, in some BP and NPK derivatives, it is shown that the excited singlet states are reactive for ω -cleavage,³⁷ or that the quantum yields depend on the excitation wavelength.^{39,40} It has been revealed that the reactivity of ω -bond cleavage is closely related to the spin multiplicity and electronic character of the excited states, bond enthalpies and leaving groups. We have studied ω -cleavage at the para-position of benzophenones. Since benzophenone is one of the most fundamental compounds in photochemical and photobiological investigations, its photophysical processes are well understood through pico- and nano-second time-resolved measurements.⁴¹ The lowest excited triplet state (T_1) of benzophenone is produced within 10 ps in solution due to a fast intersystem crossing upon photoexcitation. It does not seem that the substitution with alkyl groups at the paraand meta-positions affects the photophysics for triplet formation. It is reported that photolysis of 2-methylbenzophenone efficiently provides the corresponding triplet, which readily undergoes intramolecular H-atom abstraction.42,43 However, the effect of the substituted position to ω-cleavage of benzophenones has not been examined.

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In the present study, photoinduced ω -bond dissociation in *meta*-substituted halomethylbenzophenones (*m*-HMBP) was examined by laser photolysis techniques. It is revealed that the substituted position on HMBP affects the reactivities of ω -cleavage in the lowest excited singlet and triplet states. The differences in these reactivities are rationalized with the aid of DFT calculations.

2. Experimental

m-Methylbenzophenone (*m*-MBP) was purchased commercially. m-Chloromethylbenzophenone (m-CMBP) was synthesized by a reaction of *m*-MBP with sulfuryl chloride in CCl₄ in the presence of benzoyl peroxide. *m*-Bromomethylbenzophenone (m-BMBP) was synthesized by a reaction of m-MBP with N-bromosuccinimide in benzene in the presence of benzoyl peroxide. m-Halomethylbenzophenones (m-HMBP; m-BMBP and *m*-CMBP) were purified by repeated recrystallizations from hexane. Acetone (Ac), acetonitrile (ACN), methanol, ethanol and butyronitrile were distilled for purification. Diethyl ether (spectroscopy grade, Kanto) and isopentane (spectroscopy grade, Fluka) were used as supplied. ACN and butyronitrile were used as the solvents at 295 K while EPA (diethyl ether-isopentane-ethanol, 5:5:2 v/v/v) and a mixture of methanol and ethanol (1 : 1 v/v) were used as matrices at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively.

Time-resolved EPR measurements were carried out using an X-band EPR spectrometer (Varian E-109E) without magnetic field modulation as reported previously.⁴⁴ A XeCl excimer laser (Lambda Physik COMPex 102, 308 nm, 20 Hz) was used as a pulsed light source. Sample solutions for the CIDEP measurements were constantly deoxygenated by argon gas bubbling and flowed into a quartz cell in the EPR resonator.

All the samples for transient absorption measurements were degassed in a quartz cell with a 1 cm path length by several freeze-pump-thaw cycles on a high vacuum line. The concentration of *m*-HMBP for 266 nm laser photolysis was adjusted to achieve the optical density at 266 nm being ca. 0.7 in ACN. Transient absorption measurements were carried out at 295 K. Fourth harmonics (266 nm) of a Nd³⁺:YAG laser (JK Lasers HY-500; pulse width 8 ns) and a XeCl excimer laser (308 nm; Lambda Physik, Lextra 50; pulse width 20 ns) at 308 nm were used for flash photolysis. The number of the repetition of laser pulsing in a sample was less than four pulses to avoid excess exposure. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.⁴⁵ The transient data obtained by laser flash photolysis was analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku with which one can take a transient absorption spectrum with a one-shot laser pulse.

Electronic-state energy and geometry calculations were performed using density functional theory (DFT) and timedependent DFT (TDDFT) with a Becke style three-parameter hybrid exchange functional and Lee Yang Parr correlation functional (B3LYP).⁴⁶ Polarized valence triple-ζ basis sets were employed for the calculations: 6-311G(d) for C, H, O, and Cl atoms and lanl2dzdp for the Br atom in which the inner-shell electrons being replaced by Los Alamos relativistic effective core potential.⁴⁷ In calculation of the potential energy curves of ω -cleavage, the geometrical optimizations for the lowest triplet (T₁) states were performed at an unrestricted DFT level with a triplet spin multiplicity using the Gaussian 03 program package,⁴⁸ while the geometry of the lowest singlet (S₁) states was calculated using the analytical TDDFT gradient with the TURBOMOLE 5.7 program package.⁴⁹ Atomic spin densities, SD on a C(α) were computed using Mulliken population analysis of the atomic orbitals of T₁ states. All quantum chemical calculations were carried out on a labdeveloped PC cluster system consisting of 32 Pentium IV CPUs (3.0–3.4 GHz).

3. Results

3.1 Absorption and emission measurements

Fig. 1 shows absorption spectra of *m*-MBP, *m*-BMBP and *m*-CMBP in ACN at 295 K and their phosphorescence spectra in EPA glass at 77 K. They are similar to each other. It was confirmed that the phosphorescence excitation spectra agreed well with the corresponding absorption spectra. From the phosphorescence origins, the energy levels of the lowest triplet (T₁) states of *m*-MBP, *m*-CMBP and *m*-BMBP were determined to be 68.9 kcal mol⁻¹. From the similarity in the phosphorescence spectra of *m*-CMBP and *m*-BMBP with that of *m*-MBP, it is inferred that the electronic character of the lowest excited triplet state of *m*-CMBP and *m*-BMBP is of n,π^* .

3.2 Direct excitation

Fig. 2 shows transient absorption spectra obtained after 266 nm laser pulsing in the degassed ACN solutions of *m*-MBP, *m*-CMBP and *m*-BMBP at 295 K, respectively. The transient absorption spectra at 100 ns for *m*-MBP and *m*-CMBP are due to the triplet states of *m*-MBP and *m*-CMBP since they are similar to that of benzophenone. The transient absorption spectrum having the absorption maximum at 335 nm observed at 100 ns for *m*-BMBP, however, cannot be due to triplet *m*-BMBP, but should be assigned to that of the *m*-benzoylbenzyl



Fig. 1 Absorption spectra in ACN at 295 K and phosphorescence spectra in a mixture of methanol and ethanol (1 : 1 v/v) at 77 K for (a) *m*-MBP, (b) *m*-CMBP and (c) *m*-BMBP.



Fig. 2 (a) A transient absorption spectrum observed at 100 ns after 266 nm laser pulsing in the ACN solution of *m*-MBP. (b) Transient absorption spectra observed at 100 ns (broken line) and 1 μ s (solid line) after 266 nm laser pulsing in the ACN solution of *m*-CMBP. Inset: a temporal absorbance change at 335 nm in the presence of the dissolved oxygen in the ACN solution. (c) A transient absorption spectrum observed at 100 ns after 266 nm laser pulsing in the ACN solution of *m*-BMBP.

radical (*m*-BBR) since it resembles the absorption spectrum of the *p*-benzoylbenzyl radical (*p*-BBR) having a molar absorption coefficient of $7600 \pm 400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ at 320 nm.^{36,37} As with *m*-CMBP, when triplet *m*-CMBP was quenched by the dissolved oxygen (see inset in Fig. 2b), the absorption spectrum obtained at 1 µs after 266 nm laser pulsing was similar to that of *m*-BBR. These observations that *m*-BBR was formed upon photolysis of *m*-CMBP and *m*-BMBP indicate that *m*-HMBP undergoes ω -bond dissociation to form *m*-BBR in ACN at room temperature.

The quantum yield (Φ_{rad}) of the *m*-BBR formation upon 266 nm laser photolysis of *m*-HMBP was determined with the use of eqn (1) based on the absorption change (ΔA_{335}) at 335 nm due to *m*-BBR obtained at 100 ns for *m*-BMBP and at 1 µs for *m*-CMBP in the presence of the dissolved oxygen.

$$\Phi_{\rm rad} = \Delta A_{335} \Delta \varepsilon_{335}^{-1} I_{\rm abs}^{-1} \tag{1}$$

where $\Delta \varepsilon_{335}$ and I_{abs} are, respectively, the molar absorption coefficient change of *m*-BBR at 335 nm and the number of the photon flux of a laser pulse absorbed by *m*-HMBP. The $\Delta \varepsilon_{335}$ value was assumed to be the same as that (7500 dm³ mol⁻¹ cm⁻¹) of the *p*-BBR at 320 nm.^{36,37} The quantity of I_{abs} was determined by using the absorption of triplet benzophenone (BP) in ACN as an actinometer.⁵⁰

$$I_{\rm abs} = \Delta A_{\rm T}^{\rm BP} \varepsilon_{\rm T}^{\rm BP-1} \Phi_{\rm ISC}^{\rm BP-1} \tag{2}$$

where $\Delta A_{\rm T}^{\rm BP}$, $\varepsilon_{\rm T}^{\rm BP}$ and $\Phi_{\rm ISC}^{\rm BP}$ are the initial absorbance at 520 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 520 nm in ACN (6500 dm³ mol⁻¹ cm⁻¹)⁵¹ and triplet yield of benzophenone (1.0), respectively.⁴² By using eqn (1) and (2), the $\Phi_{\rm rad}$ value was determined to be 0.085 ± 0.04 for *m*-CMBP and 0.25 ± 0.02 for *m*-BMBP.

3.3 Triplet sensitization

Triplet sensitization of Ac (1.0 mol dm^{-3}) was carried out in ACN solutions of *m*-MBP, *m*-BMBP and *m*-CMBP by using a XeCl excimer laser (308 nm). Fig. 3 shows transient absorption spectra obtained upon acetone sensitization of m-MBP, m-CMBP and m-BMBP using 308 nm laser pulse. The transient absorption spectra for the Ac-m-MBP and m-CMBP systems are due to triplet *m*-MBP and *m*-CMBP, respectively. The intensity of the absorbance at 525 nm for triplet m-MBP and at 320 nm for triplet *m*-CMBP increases according to the firstorder kinetics ($2.9 \times 10^6 \text{ s}^{-1}$ for *m*-MBP and $2.6 \times 10^6 \text{ s}^{-1}$ for *m*-CMBP) as shown in insets in Fig. 3a and b, respectively. From these observations, it can be recognized that triplet energy transfer proceeds from triplet Ac to m-MBP or *m*-CMBP to produce the corresponding triplet states. After depletion of triplet m-CMBP, no residual transient absorption was seen. This indicates that triplet *m*-CMBP does not undergo ω -cleavage. The transient absorption spectrum for the Ac-m-BMBP system obtained at the time (2.4 µs) of the



Fig. 3 (a) A transient absorption spectrum observed at 850 ns after 308 nm laser pulsing in an Ac(0.7 mol dm⁻³)–*m*-MBP(8 × 10⁻⁴ mol dm⁻³) system. Inset: a temporal absorbance change at 525 nm. (b) A transient absorption spectrum observed at 650 ns after 308 nm laser pulsing in an Ac(0.7 mol dm⁻³)/*m*-CMBP(8 × 10⁻⁴ mol dm⁻³) system. Inset: a temporal absorbance change at 320 nm. (c) A transient absorption spectrum observed at 2.4 µs after 308 nm laser pulsing in an Ac(0.7 mol dm⁻³)–*m*-BMBP(8 × 10⁻⁴ mol dm⁻³) system. Inset: a temporal absorbance change at 335 nm.



Fig. 4 (a) The rate (k_{obsd}) for the formation of triplet *m*-MBP, triplet *m*-CMBP and *m*-BBR obtained upon 308 nm laser photolysis of the Ac (0.7 mol dm⁻³)–*m*-MBP (\bigcirc), *m*-CMBP (\square) and *m*-BMBP (\bigcirc) systems, respectively, plotted as a function of [Q]. (b) The quantum yields (Φ_{TET} and Φ_{rad}^{sens}) for triplet *m*-MBP (\bigcirc) and *m*-BBR (\bigcirc) formation upon 308 nm laser photolysis of Ac–*m*-MBP and *m*-BMBP systems, respectively, plotted as a function of [Q]. The solid curves were calculated by eqn (6) and (7) for Φ_{TET} and Φ_{rad}^{sens} , respectively.

maximum absorbance at 335 nm (see inset Fig. 3c) was similar to that of *m*-BBR. In other words, *m*-BBR is generated *via* the triplet state of *m*-BMBP upon sensitization. The rise rate of the *m*-BBR formation was $1.7 \times 10^6 \text{ s}^{-1}$. The observed rates (k_{obsd}) for the triplet formation of *m*-MBP and *m*-CMBP, and the *m*-BBR formation from triplet *m*-BMBP are plotted as a function of the concentration, [Q] of the quencher, Q in Fig. 4. Since the plots give straight lines, the k_{obsd} can be formulated by

$$k_{\rm obsd} = k_0 + k_{\rm q}[\rm Q] \tag{3}$$

where k_0 and k_q , respectively, represent the decay rate of triplet acetone in the absence of the quencher and the rate constant for quenching triplet Ac by the quencher. From the intercept and slope of the line, the values of k_0 and k_q were, respectively, determined to be $8.0 \times 10^5 \text{ s}^{-1}$ and $2.9 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for *m*-MBP, $2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for *m*-CMBP and $1.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for *m*-BMBP.

The quantum yields (Φ_{TET} and $\Phi_{\text{rad}}^{\text{sens}}$) for the formation of triplet *m*-MBP and *m*-BBR from *m*-BMBP upon triplet sensi-

tization were determined by eqn (4) and (5), respectively.

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$$\Phi_{\rm TET} = \Delta A_{525}^{\rm sens} \varepsilon_{525}^{-1} I_{\rm abs}^{-1} \tag{4}$$

$$\Phi_{\rm rad}^{\rm sens} = \Delta A_{335}^{\rm sens} \Delta \varepsilon_{335}^{-1} I_{\rm abs}^{-1} \tag{5}$$

where $\Delta A_{525}^{\text{sens}}$ and $\Delta A_{335}^{\text{sens}}$ denote the maximum absorption changes due to the formation of triplet *m*-MBP at 525 nm and *m*-BBR at 335 nm, respectively (see insets in Fig. 3). The molar absorption coefficient, ε_{525} , of triplet *m*-MBP at 525 nm was determined to be 6700 dm³ mol⁻¹ cm⁻¹ by comparison with that of benzophenone (6500 dm³ mol⁻¹ cm⁻¹ at 520 nm)⁵¹ and the value 7500 dm³ mol⁻¹ cm⁻¹ was used as the molar absorption coefficient change, $\Delta \varepsilon_{335}$ of BBR at 335 nm. The value of I_{abs} at 308 nm, the photon flux absorbed by Ac, was determined by eqn (2). The obtained values of Φ_{TET} and $\Phi_{\text{rad}}^{\text{sens}}$ for the Ac-*m*-MBP and *m*-BMBP systems are plotted as a function of [Q] in Fig. 4b. Both the values nonlinearly increase with increasing [Q]. On the other hand, Φ_{TET} and $\Phi_{\text{rad}}^{\text{sens}}$ are related with the kinetic parameters, k_0 and k_q by eqn (6) and (7).

$$\Phi_{\text{TET}} = k_q [\mathbf{Q}] \alpha_{\text{TET}} \Phi_{\text{ISC}}^{\text{Ac}} (k_0 + k_q [\mathbf{Q}])^{-1} \quad \mathbf{Q} \text{ for } m\text{-}\mathbf{MBP} \quad (6)$$

$$\Phi_{\text{rad}}^{\text{sens}} = k_q [Q] \alpha_{\text{rad}}^{\text{T}} \alpha_{\text{TET}} \Phi_{\text{ISC}}^{\text{Ac}} (k_0 + k_q [Q])^{-1}$$

$$Q \text{ for } m\text{-MBP}$$

$$(7)$$

where α_{TET} , $\alpha_{\text{rad}}^{\text{T}}$ and $\Phi_{\text{ISC}}^{\text{Ac}}$ are the efficiency for triplet energy transfer from triplet Ac to *m*-MBP or *m*-BMBP, the efficiency for the radical formation in the triplet state of *m*-BMBP, and the triplet yield of Ac (1.0), respectively.⁵² By best-fitting eqn (6) and (7) to the experimental values of Φ_{TET} and $\Phi_{\text{rad}}^{\text{T}}$, respectively, with the use of the k_0 and k_q values obtained above, the α_{TET} for the Ac–*m*-MBP system was obtained to be 0.65 ± 0.03 while a product value of $\alpha_{\text{rad}}^{\text{T}}\alpha_{\text{TET}}$ for the Ac– *m*-BMBP system was determined to be 0.26 ± 0.02. By adopting the α_{TET} value (0.65) of the Ac–*m*-MBP system to the Ac–*m*-BMBP system, the $\alpha_{\text{rad}}^{\text{T}}$ value for the Ac–*m*-BMBP system is determined to be 0.40 ± 0.04. The determined $\alpha_{\text{rad}}^{\text{T}}$ values are listed in Table 1 along with those of *p*-HMBP.

3.4 DFT calculations

Fig. 5a and b show potential energy curves in *m*-BMBP and *m*-CMBP, respectively, calculated as a function of the distance between the benzylic carbon and the halide atom, X, d(C-X). These curves were obtained from constrained geometry optimizations for the S₁ and T₁ states with the following assumptions. For the T₁ states, the angle of X–C(α)–C(4) was kept

 Table 1
 Photophysical and photochemical parameters for m-HMBP obtained in the present work^a

X	$E_{\rm T}^{\ \ b}/{\rm kcal}\ {\rm mol}^{-1}$	$k_q^{\ c}/10^9 \ dm^3 \ mol^{-1} \ s^{-1}$	$\alpha_{\rm rad}^{{\rm S}_{d}d}$	$\alpha_{\rm rad}^{\rm T}{}^{e}$	BDE(C-X) ^f /kcal mol ⁻¹	SD^g	$\Delta E_{\rm cal}^{{\rm S}~h}/{\rm kcal}~{\rm mol}^{-1}$	$\Delta E_{\rm cal}^{{\rm T}~i}/{\rm kcal}~{\rm mol}^{-1}$
Br	68.9 (n.d.) ^{<i>j</i>}	1.3 (2.9)	0.25 (0.41)	0.40 (0.53)	58.0 (53.0)	-0.009 $(0.054)^k$	$6.5 (1.2)^k$	4.6 (2.6) ^k
Cl	68.9 (68.4)	2.5 (3.7)	0.085 (~0)	0 (0.51)	70.6 (65.6)	-0.006 (0.027) ^k	$(10.9)^k$	10.7 (6.3) ^k

^{*a*} Data in parentheses are for *p*-HMBP obtained previously.^{37 *b*} Triplet energies determined from the 0–0 origins of the phosphorescence spectra at 77 K. ^{*c*} Quenching rate constants of triplet Ac by *m*-HMBP. ^{*d*} Efficiencies of the radical formation in the S₁ state. ^{*e*} Efficiencies of the radical formation in the T₁ state. ^{*f*} Bond dissociation energies of the C–X bond estimated by MP3 calculations. ^{*g*} Spin densities on the CH₂ atom at the geometry optimized for T₁. ^{*h*} Calculated activation energies for C–X bond dissociation in the T₁ state. ^{*j*} Not determined. ^{*k*} Obtained in the present work.





(a)

(b)

larger than 90° during the geometry optimization to avoid the complex formation between X radical and m-BBR. The geometry optimization for the S₁ state without any constraints revealed that the phenyl ring was perpendicular to the halomethylphenyl group whereas the dihedral angle between two phenyl rings was calculated to be about 50° for both m-HMBP in the ground state and *m*-BBR. Since it is presumably hard for such a large rotation of the phenyl ring to occur in solution within the very short lifetime of the S₁ state (a few picoseconds),¹ the dihedral angle between two phenyl rings was kept equal to or greater than 50° for the geometry optimization. From the potential energy curves, the activation energies for the ω -cleavage in the S₁ and T₁ states (ΔE_{cal}^{S} and ΔE_{cal}^{T}) respectively) were estimated as the difference in potential energy between the excited state and the transition state (TS) which gives the maximum when the C-X bond is elongated. The ΔE_{cal}^{S} and ΔE_{cal}^{T} values are listed in Table 1.

The bond dissociation energy of the C-X bond in m-HMBP, BDE(C-X) was obtained on the basis of the heat of formation $(\Delta_{\rm f} H)$ for *m*-BMBP and *m*-CMBP. *m*-BBR and halogen atoms (X = Br and Cl) computed using a semi-empirical PM3 program contained in MOPAC 97. These were $\Delta_{\rm f} H$ (m-BMBP) = $15.5 \text{ kcal mol}^{-1}$, $\Delta_f H (m\text{-CMBP}) = 5.2 \text{ kcal mol}^{-1}$, $\Delta_{\rm f} H (m\text{-BBR}) = 46.8 \text{ kcal mol}^{-1}, \Delta_{\rm f} H (\text{Br}^{\bullet}) = 26.7 \text{ kcal mol}^{-1},$ and $\Delta_{\rm f} H$ (Cl[•]) = 29.0 kcal mol⁻¹. The BDE(C–X) value is calculated to be 58.0 kcal mol^{-1} for *m*-BMBP and 70.6 kcal mol^{-1} for *m*-CMBP by using eqn (8).

$$\begin{split} \Delta_{\rm f} H(m\text{-}{\rm HMBP}) &= \Delta_{\rm f} H(m\text{-}{\rm BBR}) \\ &+ \Delta_{\rm f} H({\rm X}^{\bullet})\text{-}{\rm BDE}({\rm C-X}) \end{split} \tag{8}$$

Discussion 4.

Spin multiplicities of dissociative states 4.1

Transient absorption measurements upon laser flash photolysis of *m*-CMBP and *m*-BMBP in the present work show that they undergo ω-cleavage to generate *m*-BBR. Triplet sensitiza-

tion of *m*-HMBP proves that the T_1 state of *m*-BMBP is dissociative while that of *m*-CMBP is inert to decomposition. From the observations for *m*-CMBP, it is concluded that the C-Cl bond of *m*-CMBP cleaves only in the excited singlet state, and that the dissociation process competes with intersystem crossing to the triplet manifold. With *m*-BMBP, formation of the triplet state was not observed in transient absorption upon direct excitation at room temperature, and CIDEP signal was absent upon 308 nm laser photolysis of m-BMBP. The absence of CIDEP signal suggests that the m-BBR formation upon photolysis of m-BMBP is not contributed from the bond-dissociative triplet manifold. It should be noted that photolysis of p-CMBP shows net-emissive CIDEP due to *p*-BBR because the C–Cl bond cleaves in the triplet state.³⁷ The large spin-orbit coupling interaction of the halogen atom eliminates the electron spin polarization due to the radical pair mechanism, even if the spin polarization is created during the interaction between the pair radicals in the solvent cage.^{25a} Based on these photolytic results of *m*-BMBP, it seems that deactivation processes of the S_1 state of *m*-BMBP are governed by the efficient C-Br bond dissociation, which may hamper intersystem crossing from the S_1 to the triplet state of *m*-BMBP at room temperature.

4.2 Efficiencies of ω-cleavage

We have determined the quantum yields, Φ_{rad} of the free radical formation upon direct excitation of m-HMBP. As mentioned above, the m-BBR formation from photoexcited *m*-HMBP originates from the C-X bond dissociation in the S₁ state. The actual efficiencies for the C-X bond rupture in the S_1 states are, however, unable to be determined with our nanosecond laser system since some of the singlet radical pairs produced in solvent cages may undergo the fast geminate recombination within the laser pulse duration (ca. 20 ns). Values of these efficiencies should be larger than those of the $\Phi_{\rm rad}$ obtained. In contrast, values of efficiencies, $\alpha_{\rm cal}^{\rm S}$ for free radical formation due to the C–X bond fission in the S_1 state can be regarded as being equal to those of the obtained quantum yields, Φ_{rad} since the C-X bond cleaves only in the S₁ state upon direct photoexcitation of *m*-HMBP. Here, we assume the same efficiency of the geminate recombination of the in-cage singlet biradical pair formed in the S₁ states between *m*- and *p*-BMBPs. The α_{cal}^{S} value (0.25) of *m*-BMBP is smaller than that of p-BMBP (0.41).³⁷ The S₁ state of *m*-CMBP is reactive for ω -cleavage ($\alpha_{cal}^{S} = 0.085$) while that of *p*-CMPB is inert ($\alpha_{cal}^{S} \sim 0$).³⁷ Based on these α_{cal}^{S} values, effects of substituted positions in HMBPs to ω-cleavage are recognized.

When the C-Br bond dissociates in the triplet state of *m*-BMBP, a triplet radical pair, ${}^{3}(m$ -BBR + Br ${}^{\bullet})_{cage}$ of *m*-BBR and Br radical may be initially produced in a solvent cage according to the spin conservation rule. Because of the large spin-orbit coupling interaction due to the heavy Br atom, the singlet-triplet (S-T) mixing may be efficient to the triplet incage biradical pair to some extent. The triplet radical pair escapes from the solvent cage competing with the S-T mixing that results in geminate recombination. Thus, the α_{rad}^{T} value (0.40) should be smaller than that of the intrinsic efficiency of the C-Br bond rupture in the triplet manifold of *m*-BMBP.

The residual efficiency $(1 - \alpha_{rad}^{T} = 0.60)$ should be due to intersystem crossing from the T₁ to the ground state and the geminate recombination induced by the heavy Br atom. When we compare the α_{rad}^{T} values between *m*- and *p*-BMBPs hereafter, we assume the same ratio of the rate for the escape of the triplet in-cage radical pair from the solvent cage to the rate for the geminate recombination of the singlet in-cage radical pair converted from the triplet radical pair by the S–T mixing due to the heavy atom effect.

4.3 Energy diagrams for excited states of *m*-HMBP

Based on the experimental results obtained, energy diagrams for the deactivation processes including the C-X bond cleavage of photoexcited *m*-CMBP and *m*-BMBP are depicted in Scheme 1. The dissociation mechanism in the excited states of aromatic molecules can be interpreted to be a thermally activated crossing of the reactive excited state with dissociative potential surfaces leading to free radicals.²³ The electronic configurations of the plausible potentials for the C-X bond rupture in *m*-HMBP are of π, σ^* and σ, σ^* . It was originally suggested that radical cleavages of excited states proceed by avoided crossings between states of the same overall symmetry.^{53,54} In the present case, the S_1 and T_1 states of n,π^* would correlate with the corresponding singlet and triplet π,σ^* potentials. With the diagram for *m*-CMBP in Scheme 1, the $S_1(n,\pi^*)$ undergoes C-Cl bond cleavage along the correlated singlet π, σ^* potential to produce *m*-BBR and Cl[•]. This process is competitive with intersystem crossing to the T_1 state where the C-Cl bond does not dissociate. The lifetime of the S₁ state of benzophenone is known to be as short as 10 ps,⁴¹ the rate of ω -cleavage from the S₁ state of *m*-CMBP is of the magnitude of 10^9-10^{10} s⁻¹. The absence of bond cleavage in the T₁ state $(\alpha_{rad}^{T} = 0)$ may be due to the BDE (70.6 kcal mol⁻¹) for the C-Cl bond being slightly larger than the triplet energy (68.9 kcal mol⁻¹), which may yield a large activation barrier, ΔE to a dissociative triplet π, σ^* potential. The triplet state of *m*-CMBP is fated to deactivate only by intersystem crossing to the ground state. It is noteworthy that the reactivities in the S_1 and T1 states of m-CMBP toward ω -cleavage of the C-Cl bond differ from those of *p*-CMBP ($\alpha_{cal}^{S} \sim 0$ and $\alpha_{rad}^{T} = 0.51$).³⁷ On the other hand, the S_1 state of *m*-BMBP does not deactivate

via intersystem crossing, but undergoes the C–Br bond scission to produce *m*-BBR and Br radical with an efficiency (α_{cal}^{S}) of 0.25, which is smaller than that of *p*-BMBP (0.41).³⁷ Triplet sensitization has shown that the T₁ state also undergoes ω -cleavage of the C–Br bond with a smaller efficiency $(\alpha_{rad}^{T} = 0.40)$ than that of triplet *p*-BMBP (0.53).³⁷ It is revealed that the S₁ and T₁ states of *m*-BMBP are reactive toward ω -bond dissociation as well as those of *p*-BMBP.

4.4 Understanding of substituted position effects based on DFT calculations

DFT calculations for HMBP demonstrate the presence of activation energies, ΔE_{cal}^{S} and ΔE_{cal}^{T} for ω -bond dissociation. Since energy barriers between excited states and dissociative potential surfaces are essential for photoinduced bond rupture, we can elucidate the relationship between the activation energies and efficiencies of ω -cleavage. At first, the ΔE_{cal}^{S} value (6.5 kcal mol⁻¹) of *m*-BMBP is much larger than that of *p*-BMBP (1.2 kcal mol⁻¹). The smaller ω -cleavage efficiency (0.25) in the S₁ state of *m*-BMBP than that of *p*-BMBP (0.41)can be explained by this difference in the ΔE_{cal}^{S} value. The activation energy may also facilitate the reaction in the T_1 state of BMBPs. The larger ΔE_{cal}^{T} value (4.6 kcal mol⁻¹) for *m*-BMBP than that for *p*-BMBP (2.6 kcal mol⁻¹) corresponds to the smaller α_{rad}^{T} value (0.40) for *m*-BMBP than that for *p*-BMBP (0.53). The other factor to affect the α_{rad}^{T} values of BMBPs may be spin densities, SD, on the CH2 group at the T_1 geometry, which would correlate with the spin density of a σ^* orbital for the C–X bond. The calculated SD values are listed in Table 1. Squared values of SD are efficient in comparison. The fact that the squared SD value for triplet m-BMBP is smaller than that for triplet p-BMBP indeed rationalizes the smaller ω-cleavability. In contrast, comparison with SD values would be less useful for triplet CMBPs. The BDE value (70.6 kcal mol⁻¹) for *m*-CMBP is obviously larger than the triplet energy (68.9 kcal mol⁻¹). Since ω -cleavage is absent in triplet *m*-CMBP, there would be a large activation energy for the C–Cl bond dissociation shown as ΔE in Scheme 1. In fact, the calculated ΔE_{cal}^{T} value (10.7 kcal mol⁻¹) for m-CMBP is larger than that for triplet p-CMBP (6.3 kcal mol⁻¹) where ω -cleavage efficiently proceeds. Finally, the



Scheme 1 Schematic energy diagrams for the deactivation and bond dissociation processes of excited *m*-CMBP (left) and *m*-BMBP (right).

difference in ΔE_{cal}^{s} of CMBPs cannot be understood from the DFT calculation data. The ΔE_{cal}^{S} value of *m*-CMBP (13.0 kcal mol^{-1}) is relatively larger than that of *p*-CMBP (10.9 kcal mol^{-1}). ω -Bond dissociation is, however, recognized to take place in the S_1 state of *m*-CMBP whereas it is absent from triplet *p*-CMBP. The electronic character and state energy of the S₁ states of both *m*- and *p*-CMBPs are similar. Concerning C-Cl bond cleavage in the S_1 state, the BDE(C-Cl) values differ by 5 kcal mol^{-1} between *m*- and *p*-CMBPs. From this consideration, it is inferred that the degree of correlation between the S_1 state and the corresponding dissociative ${}^{1}(\pi,\sigma^{*})$ potential surface is affected by the BDE value. There would be no interaction between the S₁ state and (π,σ^*) potentials for p-CMBP (unavoided crossing) while a weak avoided crossing may cause between the potential curves for *m*-CMBP due to the relatively large BDE(C-Cl).

5. Conclusions

Photochemical properties of ω -bond cleavage in *m*-HMBP have been studied by laser photolysis techniques and DFT calculations. Based on the efficiencies of free radical formation, it is shown that reactivity of ω-cleavage clearly depends on the substituted positions of HMBPs. The reaction processes and efficiencies of ω -cleavage in excited *m*-HMBP have been rationalized with the aid of DFT calculations. With m-CMBP, ω -cleavage does not occur in the T₁ state, but it does in the S₁ state. The dissociation process in the S_1 state of *m*-CMBP competes with intersystem crossing to the T₁ state. The absence of dissociation in the T1 state of m-CMBP is explained in terms of a large activation energy, ΔE_{cal}^{T} originated from the BDE(C-Cl) being larger than the triplet energy. These properties of *m*-CMBP are quite contrary to the reactivity towards ωcleavage in p-CMBP. In contrast to CMBP, both the S₁ and T₁ states of *m*-BMBP are reactive to ω -cleavage without intersystem crossing from the S_1 to T_1 states. These properties are similar to those of p-BMBP. Substituted position effects between *m*-BMBP and *p*-BMBP are shown as a reduction in the efficiencies, α_{cal}^{S} and α_{rad}^{T} . It seems that the α_{cal}^{S} values of BMBPs are affected by an activation barrier, ΔE_{cal}^{S} whereas spin densities on a σ^* orbital of the C–Br bond are crucial to the reactivity of ω -cleavage in the T₁ states of BMBPs.

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References

- N. J. Turro, Modern Molecular Photochemistry, Benjamin/Cummings Publishing Co., Menlo Park, CA, 1978.
- 2 A. Gilbert and J. Baggott, in *Essentials of Molecular Photochem-istry*, ed. P. J. Wagner, Blackwell Scientific Publications, Oxford, 1991.
- 3 A. Schönberg, A. K. Fateen and S. M. A. R. Omran, J. Am. Chem. Soc., 1956, 78, 1224.

- 4 C. L. MacIntosh, P. de Mayo and R. W. Yip, *Tetrahedron Lett.*, 1967, 37.
- 5 J. R. Collier and J. Hill, Chem. Commun. (London), 1968, 700.
- 6 (a) H. Shizuka, Bull. Chem. Soc. Jpn., 1968, 41, 2343; (b) H. Shizuka and I. Tanaka, Bull. Chem. Soc. Jpn., 1969, 42, 52; (c) H. Shizuka, T. Morita, Y. Mori and I. Tanaka, Bull. Chem. Soc. Jpn., 1969, 42, 1831.
- 7 D. G. Whitten and W. E. Punch, Mol. Photochem., 1970, 2, 77.
- 8 F. R. Stermitz, D. E. Nicodem, V. P. Muralidharan and C. M. O'Donnell, *Mol. Photochem.*, 1970, 2, 87.
- 9 M. C. Caserio, W. Lauer and T. Novinson, J. Am. Chem. Soc., 1970, 92, 6082.
- 10 S. Majeti, Tetrahedron Lett., 1971, 2523.
- (a) P. J. Wagner, Acc. Chem. Res., 1971, 4, 168; (b) P. J. Wagner, P. A. Kelso and A. E. Kemppainen, Mol. Photochem., 1970, 2, 81; (c) P. J. Wagner and M. J. Lindstrom, J. Am. Chem. Soc., 1987, 109, 3062.
- 12 H. Heine, J. J. Rosenkranz and H. Rudolph, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 974.
- 13 J. R. Grunwell, N. A. Marron and S. Hanhan, J. Org. Chem., 1973, 38, 1559.
- 14 F. D. Lewis, C. H. Hoyle and J. G. Magyar, J. Org. Chem., 1975, 40, 488.
- 15 G. Brunton, H. C. McBay and K. U. Ingold, J. Am. Chem. Soc., 1977, 99, 4447.
- (a) J. C. Scaiano, M. J. Perkins, J. W. Sheppard, M. S. Platz and R. L. Barcus, J. Photochem., 1983, 21, 137; (b) J. C. Netto-Ferreira, W. L. Leigh and J. C. Scaiano, J. Am. Chem. Soc., 1985, 107, 2617; (c) W. G. McGimpsey and J. C. Scaiano, Can. J. Chem., 1988, 66, 1474; (d) J. C. Scaiano, J. C. Netto-Ferreira and V. Wintgens, J. Photochem. Photobiol., A, 1991, 59, 265.
- 17 M. A. Fox and C. A. Triebel, J. Org. Chem., 1983, 48, 835.
- T. Wismontski-Kinittel and T. Kilp, *J. Phys. Chem.*, 1984, 88, 110.
 E. N. Step, V. F. Tarasov, A. L. Buchachenko and N. J. Turro, *J. Phys. Chem.*, 1993, 97, 363.
- 20 W. J. Leigh, J.-A. H. Banisch and M. S. Workentin, J. Chem. Soc., Chem. Commun., 1993, 988.
- 21 M. Hall, L. Chen, C. R. Pandit and W. G. McGimpsey, J. Photochem. Photobiol., A, 1997, 111, 27.
- 22 Y. Kaneko, S. Hu and D. C. Neckers, J. Photochem. Photobiol., A, 1998, 114, 173.
- 23 S. A. Fleming and J. A. Pincock, *Mol. Supramol. Photochem.*, 1999, 3, 211.
- 24 S. Jockusch, M. S. Landis, F. Beat and N. J. Turro, *Macromole*cules, 2001, 34, 1619.
- 25 (a) T. Suzuki, Y. Kaneko, K. Maeda, T. Arai, K. Akiyama and S. Tero-Kubota, *Mol. Phys.*, 2002, **100**, 1469; (b) T. Suzuki, Y. Kaneko, M. Ikegami and T. Arai, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 801.
- 26 (a) X. Allonas, J. Lalevée and J.-P. Fouassier, J. Photochem. Photobiol., A, 2003, 159, 127; (b) X. Allonas, J. Lalevée and J.-P. Fouassier, J. Photopolym. Sci. Technol., 2004, 17, 29.
- 27 X. Cai, P. Cygon, B. Goldfuss, A. G. Griesbeck, H. Heckroth, M. Fujitsuka and T. Majima, *Chem.-Eur. J.*, 2006, **12**, 4662.
- 28 (a) M. Yamaji, S. Wakabayashi, K. Fukuda, S. Inomata and S. Tobita, J. Photochem. Photobiol., A, 2006, 184, 86; (b) M. Yamaji, S. Wakabayashi and S. Tobita, Res. Chem. Intermed., 2006, 32, 749.
- 29 E. J. Baum and J. N. Pitts, Jr, J. Phys. Chem., 1966, 70, 2066.
- 30 (a) P. J. Wagner, J. Sedon, C. Waite and A. Gudmundsdottir, J. Am. Chem. Soc., 1994, 116, 10284; (b) P. J. Wagner and C. I. Waite, J. Am. Chem. Soc., 1995, 117, 7388; (c) P. J. Wagner, J. H. Sedon and A. Gudmundsdottir, J. Am. Chem. Soc., 1996, 118, 746.
- 31 (a) L. Thijs, S. N. Gupta and D. C. Neckers, J. Org. Chem., 1979,
 23, 4123; (b) E. A. Morlion, M. D. Bohorquez, D. C. Neckers and M. A. J. Rodger, J. Am. Chem. Soc., 1991, 113, 3599; (c) B. K. Shah and D. C. Neckers, J. Org. Chem., 2002, 67, 6117; (d) B. K. Shah, A. Gusev, M. A. J. Rogers and D. C. Neckers, J. Phys. Chem. A, 2004, 108, 5926; (e) B. K. Shah and D. C. Neckers, J. Am. Chem. Soc., 2004, 126, 1830.
- 32 T. Autrey, Ch. Devadoss, B. Sauerwein, J. A. Franz and G. B. Schuster, J. Phys. Chem., 1995, 99, 869.
- 33 A. Wrzyszczynski, J. Bartoszewicz, G. L. Hug, B. Marciniak and J. Paczkowski, J. Photochem. Photobiol., A, 2003, 155, 253.

- 34 (a) D. A. Tasis, M. G. Siskos and A. K. Zarkadis, *Macromol. Chem. Phys.*, 1998, **199**, 1981; (b) A. K. Zarkadis, V. Georgakilas, G. P. Perdikomatis, A. Trifonov, G. G. Gurzadyan, S. Skoulika and M. G. Siskos, *Photochem. Photobiol. Sci.*, 2005, **4**, 469.
- (a) X. Cai, M. Sakamoto, M. Hara, S. Inomata, M. Yamaji, S. Tojo, K. Kawai, M. Endo, M. Fujitsuka and T. Majima, *Chem. Phys. Lett.*, 2005, **407**, 402; (b) X. Cai, M. Sakamoto, M. Yamaji, M. Fujitsuka and T. Majima, *J. Phys. Chem. A*, 2005, **109**, 5989.
 M. Yamaji, T. Yoshihara, T. Tachikawa, S. Tero-Kubota, S.
- 36 M. Yamaji, T. Yoshihara, T. Tachikawa, S. Tero-Kubota, S. Tobita, H. Shizuka and B. Marciniak, J. Photochem. Photobiol., A, 2004, 162, 513.
- 37 M. Yamaji, A. Suzuki, F. Ito, S. Tero-Kubota, S. Tobita, H. Shizuka and B. Marciniak, J. Photochem. Photobiol., A, 2005, **170**, 253.
- 38 M. Yamaji, S. Inomata, S. Nakajima, K. Akiyama, S. Tobita and B. Marciniak, J. Phys. Chem. A, 2005, 109, 3843.
- 39 M. Yamaji. S. Inomata, S. Nakajima, K. Akiyama, S. Tero-Kubota, S. Tobita and B. Marciniak, *Chem. Phys. Lett.*, 2006, 417, 211.
- 40 M. Yamaji, M. Ogasawara, S. Inomata, S. Nakajima, S. Tero-Kubota, S. Tobita and B. Marciniak, J. Phys. Chem. A, 2006, 110, 10708.
- 41 (a) R. W. Anderson, Jr, R. M. Hochstrasser, H. Lutz and G. W. Scott, J. Chem. Phys., 1974, 61, 2500; (b) R. W. Anderson, Jr, R. M. Hochstrasser, H. Lutz and G. W. Scott, Chem. Phys. Lett., 1978, 28, 153; (c) D. E. Damschen, C. D. Merritt, D. L. Perry, G. W. Scott and L. D. Telly, J. Phys. Chem., 1978, 82, 2268.
- 42 A. Ishida, K. Yamamoto and S. Takamuku, Bull. Chem. Soc. Jpn., 1991, 65, 3186.
- 43 (a) T. Suzuki, U. Okuyama and T. Ichimura, *Chem. Phys. Lett.*, 1997, **266**, 107; (b) T. Suzuki, T. Omori and T. Ichimura, *J. Phys. Chem. A*, 2000, **104**, 11671; (c) T. Suzuki and T. Ichimura, *Anal. Sci.*, 2001, **17**, s23.
- 44 S. Tero-Kubota, K. Akiyama, T. Ikoma and Y. Ikegami, *J. Phys. Chem.*, 1991, **95**, 766.
- 45 M. Yamaji, Y. Aihara, T. Itoh, S. Tobita and H. Shizuka, J. Phys. Chem., 1994, 98, 7014.

- 46 (a) A. D. Becke, J. Chem. Phys., 1993, 98, 5648; (b) A. D Becke, Phys. Rev. A, 1988, 38, 3098; (c) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B, 1988, 37, 785.
- 47 C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert and L. S. Sunderlin, *J. Phys. Chem. A*, 2001, **105**, 8111.
- 48 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN 0.3 (Revision D.02), Gaussian, Inc., Wallingford, CT, 2004.
- 49 R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **165**, 162.
- 50 M. Yamaji, T. Sekiguchi, M. Hoshino and H. Shizuka, J. Phys. Chem., 1992, 96, 9353.
- 51 R. V. Bensasson and J. C. Gramain, J. Chem. Soc., Faraday Trans. 1, 1980, **76**, 1801.
- 52 M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, CRC Press, Boca Raton, FL, 3rd edn, 2006.
- 53 W. G. Dauben, L. Salem and N. J. Turro, *Acc. Chem. Res.*, 1975, **8**, 41.
- 54 J. Michl and V. Bonačić-Koutecký, *Electronic Aspects of Organic Photochemistry*, Wiley, New York, 1990.