



Non-thermal reaction triggered by a stimulated Raman process using 5-fs laser pulses in the electronic ground state: Claisen rearrangement of allyl phenyl ether

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ARTICLE INFO

Article history:

Received 23 August 2010

In final form 10 November 2010

Available online 13 November 2010

ABSTRACT

The vibrational populations of allyl phenyl ether were excited by a broadband visible 5-fs laser pulse by the stimulated Raman process to promote a 'non-thermal' Claisen rearrangement reaction in the electronic ground state. Analyses of the time-resolved vibrational spectra observed in the subpicosecond region has shown that the Claisen rearrangement proceeds in the following three-step pathway: (1) weakening of the C³O bond to generate a bis-allyl intermediate, (2) formation of the weak C¹C⁵ bond results in the generation of a six-membered structure, and (3) simultaneous processes of C³O breaking and C¹C⁵ formation leading to the generation of a keto-intermediate.

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1. Introduction

A reaction in the electronic ground state can be initiated by thermal excitation, i.e., by activation of molecular vibrations to overcome the reaction barrier. This contrasts to a photochemical reaction, which proceeds after reaching one of the electronic excited states.

Many researchers triggered thermal reactions by photo-irradiation by converting photon energy to thermal energy. These attempts resulted in the development of laser temperature-jump techniques [1–8], which enabled the studies on fast reaction kinetics in the time scales of picoseconds to microseconds. This process can be regarded as an 'incoherent' thermal reaction process. For instance, protein water solutions heated by energy from a laser pulse acted as transducers by releasing the energy as heat to cause the temperature-jump with a time resolution of 70 ps [5].

After the discovery in 1986 [9,10] that microwave irradiation shortens reaction rates and drastically improves chemical yields, numerous studies on organic syntheses by microwave irradiation have been reported [11–14]. Several researchers suggested a possibility of 'non-thermal microwave effects,' including activation of molecular vibrations [15,16]. It is thus conceivable that photo-excitation of molecular vibrations by femtosecond laser pulses can trigger reactions in the electronic ground state [17,18]. Irradiation by a broadband ultrashort pulse, whose photon energy is much lower than the lowest electronic excitation energy, can cause

a transition to vibrationally excited states of the electronic ground state by the stimulated Raman process.

Available for this purpose is a non-collinear optical parametric amplifier (NOPA) developed in our laboratory [19]. It can generate ultrashort visible laser pulses with a broadband spectral width extending from 525 to 725 nm. Photo-excitation by NOPA pulses causes the stimulated Raman process in a broadband frequency region to excite various vibrational modes in the electronic ground state. This enables a new non-thermal reaction induced by vibrational excitation in molecules, as we demonstrate in the present study on an intramolecular rearrangement reaction.

In 1912 Claisen discovered [3,3]-sigmatropic rearrangements of allyl aryl ethers [20], which became one of the popular sigmatropic reactions in organic syntheses. When allyl phenyl ether (APE) is heated, this rearrangement occurs to generate *ortho*-substituted phenol following the mechanism shown in Figure 1a. This rearrangement is thought to generate a keto-intermediate through a six-membered transition state by a supra-supra facial reaction following the Woodward–Hoffmann rules [21] and the frontier orbital theory [22]. This intermediate is unstable, and keto-enol tautomerization occurs to generate *ortho*-substituted phenol.

We call the usual Claisen rearrangement that occurs by thermal excitation the 'classical' Claisen rearrangement. On the other hand, Kharasch et al. reported in 1952 that photo-irradiation triggered the rearrangements of allyl phenyl and benzyl phenyl ethers in the electronic excited states; this reaction was thus called 'photochemical' Claisen rearrangement [23]. The mechanism of the latter rearrangement is shown in Figure 1b [24]. Under photo-irradiation of APE, intermediates of a radical pair (PhO[•] and CH₂CHCH₂•) are

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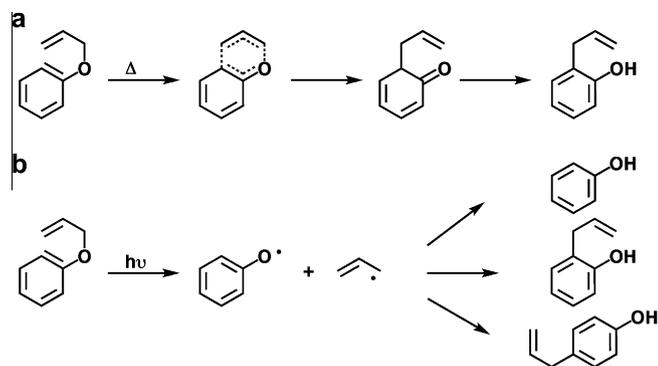


Figure 1. Schematic diagrams of (a) classical and (b) photochemical Claisen rearrangements.

generated in the electronic excited states, and a radical reaction generates the parent phenol as well as *ortho*- and *para*-substituted phenols.

In the present study, a 5-fs visible pulse laser was used to excite the vibrational modes of APE in the electronic ground state by the stimulated Raman process to trigger the Claisen rearrangement. Spectroscopic analyses of the time-resolved signals revealed the existence of a six-membered structure. The real-time changes in the vibrational modes indeed follow the reaction scheme of the classical Claisen rearrangement and revealed a detailed three-step molecular process (Figure 1a).

2. Experimental

Allyl phenyl ether (CAS: 1746-13-0), purchased from Tokyo Chemical Industry, was stored in a glass cell (400 mm³) for use as a neat sample at 295 ± 1 K. The pump–probe experiments were performed using 5-fs laser pulses [19] in the range of 525–725 nm. The pulses were generated by compressing the output from a NOPA seeded by a white-light continuum. The pump source of the NOPA was a regenerative amplifier (Spectra-Physics, model Spitfire) with a pulse duration of 100 fs with a central wavelength of 790 nm, and a repetition rate of 5 kHz. The polarizations of the pump and probe pulses were parallel to each other. The experiment was performed at the pump and probe pulse intensities of 150 and 25 μW, respectively. The focal areas of the pump and probe laser pulses were 100 and 75 μm², respectively.

The probe pulse was dispersed by a polychromator (300 grooves/mm, blazed at 500 nm) and guided to avalanche photodiodes (APDs) via a 128-channel fiber bundle. The time-resolved difference transmittance, ΔT , was measured simultaneously by APDs in the range of 525–725 nm. The signal-to-noise ratio was improved by coupling the signals of APDs to a 128-channel lock-in amplifier.

3. Results and discussion

Our objective is to excite the vibrational modes in the electronic ground state by ultrashort pulses by the stimulated Raman process and to observe non-thermal reactions occurring in the excited vibrational modes. In the first step, we confirmed that the stimulated Raman process of APE excited vibrational modes in the *electronic ground state* (Section 3.1). Then the results of the time-resolved vibrational analyses revealed appearance of the vibrational modes of reaction intermediates of the Claisen rearrangement that proceeded in these vibrationally excited states (Section 3.2). The observed real-time changes in the vibrational

frequencies indicated a three-step pathway in this rearrangement. A plausible mechanism of this reaction is discussed in Section 3.3.

3.1. Stimulated Raman excitation of vibrational modes in the ground electronic state

3.1.1. Scheme of laser-induced excitation

Allyl phenyl ether has an absorption peak at shorter wavelengths than 280 nm (Figure 2a), which is inaccessible by one-photon absorption of the visible 5-fs pulses (from 525 to 725 nm, Figure 2b) due to a small cross section. Therefore, the 5-fs pulses are likely to trigger molecular vibrations in the electronic ground state by the stimulated Raman process.

3.1.2. Vibrational frequencies observed in the pump–probe signal

When a sample is excited by a short pulse whose duration is shorter than the oscillation period of a molecular vibrational mode, a nuclear wave packet is generated via the impulsive stimulated Raman process. If the sample has no absorption band in the range of the laser wavelengths, the wave packet is produced only in the electronic ground state. The dynamics of the wave packets in such a transparent medium can be observed as a time-resolved difference in the refractive index, which reflects the molecular vibrations. Since the wave packet is described as a linear combination of the wave functions of several vibrational modes in the spectral bandwidth of the pumping laser pulse, it oscillates along the potential surface of the ground state with the period of the corresponding vibrational modes. The overlap between the moving wave packet in the ground state and the probe pulse induces a periodical change with a delay time, which modulates the transmission spectrum of the probe pulse.

The standard deviation of the induced absorbance difference, ΔA , oscillating around the zero absorbance change estimated in our study, was less than 0.5×10^{-4} , which is negligible in comparison with the oscillation amplitude ($\delta\Delta A$) of 3×10^{-4} (Figure 3). The deviation from zero is due to a very small accumulated steady-state population of the ground electronic state.

The oscillating component of the real-time trace was obtained by subtraction of the slow dynamics from the time-resolved ΔA trace using a high-pass filter. The fast Fourier transform (FFT) power spectrum of the oscillating component from 200 to 800 fs are shown in Figure 4a. The wavenumber resolution of the FFT power spectrum was estimated to be 16 cm⁻¹. The observed spectrum (Figure 4a) agreed well with the ordinary Raman spectrum of APE (Figure 4b), which confirms that the pump–probe observations directly reflect the molecular vibration dynamics in the electronic ground state. These spectra are assigned as listed in Table S1 in the Supplementary Information.

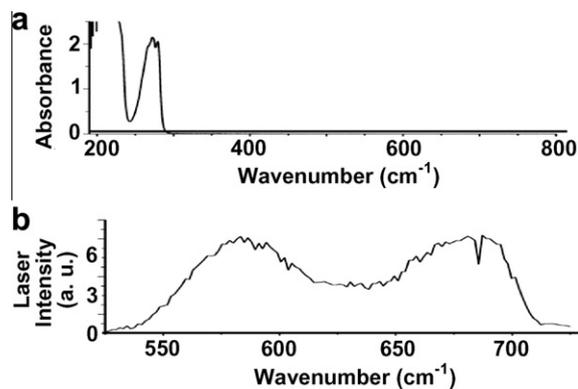


Figure 2. (a) Absorption spectrum of allyl phenyl ether and (b) the visible spectrum of the 5-fs pulse laser.

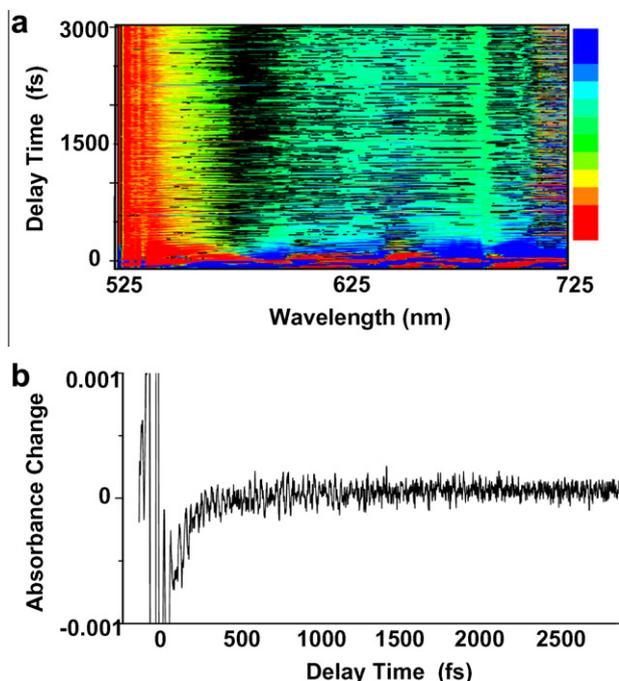


Figure 3. (a) Two-dimensional display of the absorbance change of allyl phenyl ether on the probe delay time and wavelength and (b) the real-time trace observed at 670 nm.

3.1.3. Pump power dependence of the vibrational amplitudes

Another support for the assignment was obtained from the pump-intensity dependence of the vibrational amplitude. In Figure 4c, the powers $p(i)$ of the pump-intensity dependence $I_p(i)$ for four modes were determined to be $p(815 \text{ cm}^{-1}) = 0.9 \pm 0.4$, $p(993 \text{ cm}^{-1}) = 1.0 \pm 0.1$, $p(1286 \text{ cm}^{-1}) = 0.8 \pm 0.1$, and $p(1645 \text{ cm}^{-1}) = 0.6 \pm 0.2$. The powers of $p(815 \text{ cm}^{-1})$, $p(993 \text{ cm}^{-1})$, and $p(1286 \text{ cm}^{-1})$ are mostly unity. However, that of $p(1645 \text{ cm}^{-1})$ deviates largely from unity, and it may be ascribed to contamination of higher-order terms. These results show that the observed states are not electronic excited states originating from two-photon absorption, but rather the excited vibrational levels of the electronic ground state. The linear pump-intensity dependence also suggests that the observed oscillation of ΔA is predominantly due to the wave-packet motion in the electronic ground state triggered by the stimulated Raman process.

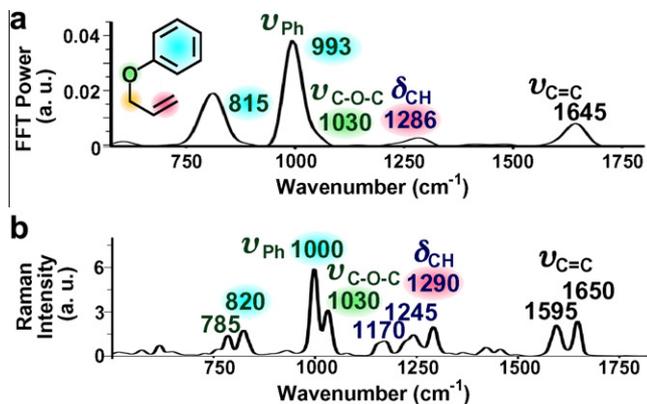


Figure 4. Vibrational spectra of allyl phenyl ether: (a) FFT power spectrum of the oscillating components of the time-resolved absorbance difference, (b) Raman spectrum, (c) probe intensity dependences of the FFT amplitude.

3.2. Observed vibrational spectra of reaction intermediates

If the above-mentioned the classical Claisen rearrangement occurs, one can observe specific changes in molecular vibrations, namely, formation of a keto-intermediate through a six-membered structure and keto-enol tautomerization. Their changes are generally expected in the classical Claisen rearrangement. If the photochemical Claisen rearrangement occurs, one would not be able to observe formation of the keto-intermediate and keto-enol tautomerization. The reason is that the radical reaction proceeds in the photochemical case (Figure 1).

In order to determine the reaction scheme, we observed the time-resolved spectra and analyzed changes in the instantaneous frequencies of the vibrational modes. The spectra were obtained by a sliding-window Fourier transformation with a Blackman window function of FWHM of 400 fs [25] (Figure 5).

After photo-excitation, only the molecular vibrational modes of the reactant APE were observed (Figures 5 and S1). Their real-time changes in the vibrational frequencies were compared with the theoretical calculation by the DFT method (B3LYP/6-311 + G**) [26] (Table 1). The time-resolved spectra showed that the Claisen

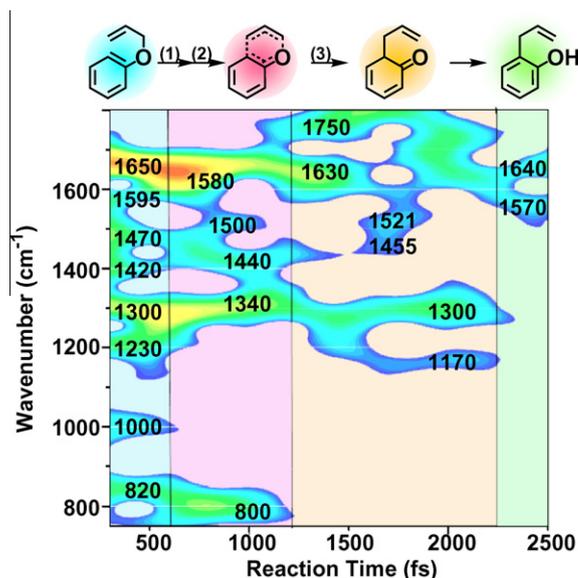


Figure 5. Observed time dependence of the vibrational spectra assigned to reaction intermediates.

Table 1
Observed and calculated vibrational wavenumbers of the chemical species involved in the Claisen rearrangement of allyl phenyl ether.

Compound ^a		Molecular vibration (cm ⁻¹)										
		ν _{C=O}		ν _{C=C}		δ _{CH₂}		δ _{CH}	ν _{C-O-C}	ν _{Ph}	δ _{Ph}	
		Allyl	Ph	Allyl	Methylene	Allyl	Methylene	Allyl	Methylene	Ether	Ph	Ph
Reactant	Exp. (Raman)			1650	1595	1460	1420	1290	1245	1030	1000	820
	Exp. (5 fs)			1650	1650	1470	1420	1300	1230	1000	1000	820
TS	Calc											
	Exp. (5 fs)			1710	1641	1461	1391	1316	1268	1052	1009	837
Keto-intermediate	Calc											
	Exp. (5 fs)			1580	1500	1440		1340				800
Phenol product	Calc			1600	1550	1437		1345				830
	Calc	1750	1630	1521	1455		1300	1170				
	Calc	1720	1699	1600	1451		1325	1220				

^a See Figure 1(a).

rearrangement triggered by the broadband ultrashort pulse proceeded in a three-step pathway as explained below.

The spectrum shows that all ν_s Ph (1000 cm⁻¹, C₆ symmetric benzene), ν_s C-O-C (1030 cm⁻¹ of the ether group, δ_{CH_2} (1230 cm⁻¹, twisting mode of the methylene group), and δ_{CH_2} (1420 cm⁻¹, wagging mode of the methylene group) signals disappear at ~700 fs. This implies that the C-O bond is either weakened or broken in the first step of the reaction. Next, the $\nu_{C=C}$ signal of the phenyl group, observed at 1595 cm⁻¹ just after photo-excitation, is red-shifted toward 1500 cm⁻¹ in the probe-delay region from 500 to 750 fs. This indicates that the six-membered structure is formed in the second step of the reaction. The observation that the $\nu_{C=C}$ signal of the allyl group, at 1650 cm⁻¹ just after photo-excitation, is red-shifted toward 1580 cm⁻¹ also supports the formation of the six-membered structure with aromatic C=C bonds. In addition, the δ_{CH_2} signal of the allyl group, at 1470 cm⁻¹ just after photo-excitation, is red-shifted toward 1440 cm⁻¹, and the δ_{CH} signal of the allyl group, at 1300 cm⁻¹ just after photo-excitation, is blue-shifted toward 1340 cm⁻¹. These are both in good agreement with the DFT results, in which the calculated δ_{CH_2} wavenumber of the allyl group is red-shifted from 1461 to 1437 cm⁻¹ and the calculated δ_{CH} wavenumber of the allyl group is blue-shifted from 1316 to 1345 cm⁻¹. A new band which can be assigned to the C=O stretching mode ($\nu_{C=O}$) appears at ~1750 cm⁻¹ after 1 ps. This verifies that the keto-intermediate is generated in the third step of the reaction. Instability of the keto-intermediate leads to keto-enol tautomerization as the final step of the reaction. Therefore, after 2 ps, the $\nu_{C=O}$ signal disappears and the phenol product is formed.

The observed frequency changes primarily support that the reaction pathway after photo-irradiation of APE by the broadband visible ultrashort pulse is equivalent to that known as the classical Claisen rearrangement (Figure 1a). Moreover, these results show that the Claisen rearrangement triggered by the broadband ultrashort pulse proceeds in the three-step pathway: (1) The C³O bond is first weakened to generate a bis-allyl intermediate. (2) Then formation of the weak C¹C⁵ bond generates a six-membered structure with aromatic CC bonds. (3) C³O breaking and C¹C⁵ formation occur simultaneously in the last step and generate the keto-intermediate, which finally proceeds to the *ortho*-substituted phenol product. Figure 6 shows a frame format of the three-step pathway with eye guide curves reflecting the bond order transition in the process.

3.3. Mechanism of vibration-induced non-thermal reaction

In the thermal reaction at temperature T , vibrational modes are randomly (incoherently) excited to the levels with energies of kT or

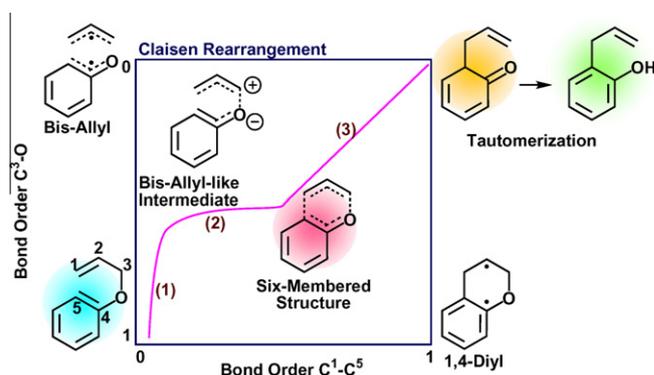


Figure 6. Transition-state profile (marked in red) determined by the time dependence of the vibrational spectra. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

lower, where k is the Boltzmann constant. Vibrational energy exchanges with high vibrational quantum numbers take place incoherently and randomly among as many as $3N-6$ modes to be dissipated, where N is the number of atoms in the molecule.

The stimulated Raman excitation by the visible laser pulse excites the molecule at high-energy vibrational levels as high as those which can be excited in the thermal excitation at ~7500 K. This is because the laser spectrum has the bandwidths of 5200 cm⁻¹ extending from 525 to 725 nm. It is different from a general method of resonant stepwise multi-photon excitation using a high-power IR laser via higher-order nonlinear interactions.

As shown in Figure 4a, however, the symmetry selection rules and the relative cross sections of the stimulated Raman process cause a selective excitation of only a small number of vibrational modes. The strongly activated modes have high vibrational quantum numbers equivalent to ~7500 K, while other modes retain much lower quantum numbers that correspond to the room temperature environment. Since the states excited by this stimulated Raman process is not thermalized just after photoexcitation, the temperature cannot be defined for such a state.

The vibrational population probably follows a Gaussian (non-Boltzmann) distribution that covers the levels up to 5200 cm⁻¹ above the ground state corresponding to the bandwidth of the 5-fs pulses. These excited vibrational populations relax within several hundreds of femtoseconds [27] to other intramolecular vibrational modes, resulting in the activation of the vibration along the reaction coordinate. This explains why the change in the structure to that of the transitional state is much faster than that in

thermally excited reactions. The activation energy of the classical Claisen rearrangement of APE was calculated by a DFT calculation (B3LYP/6-311 + G^{**}) to be ~ 35 kcal/mol, in good agreement with earlier reports [28,29]. The energy of 5200 cm^{-1} is lower than the activation energy of the classical Claisen rearrangement triggered by the thermal energy. The reason why the reaction proceeds after the stimulated Raman excitation can be explained by the following two possible mechanisms:

- (a) The reaction progresses even with activation energy lower than the classical Claisen rearrangement for activation of the vibrational mode that corresponds to the reaction coordinate in the stimulated Raman process. The vibrational modes of the six-membered structure observed in the spectrum (Figure 5) evidence that the reaction follows the scheme of the classical Claisen rearrangement (Figure 1a). However, whether or not the detailed reaction pathway to the six-membered structure is different from that of the classical Claisen rearrangement is still controversial.
- (b) Another possibility is that the stimulated Raman process generates various transition states helping the reaction to proceed below the activation energy. In any event, the detailed mechanism of the excitation process is left as an important issue for future studies.

The reason that the reaction proceeds coherently after the coherent vibration excitation by the stimulated Raman process is another nontrivial question. The transfer of vibrational coherence or even the creation of coherence that induces a chemical reaction has been discussed by Jean and Fleming [30], who simulated weak oscillations clearly observed in an electronic curve-crossing process using a multilevel formulation of Redfield's theory. The coherent progress of the reaction was also experimentally demonstrated for myoglobin [31,32].

4. Conclusion

The excited vibrational states of allyl phenyl ether were produced by the broadband visible 5-fs pulse by the stimulated Raman process. The vibrational excitation was found to induce the Claisen rearrangement reaction. The observed vibrational spectra show that the Claisen rearrangement proceeds in the following three-step pathway: (1) weakening of the C³O bond to generate the bis-allyl intermediate, (2) formation of the weak C¹C⁵ bond results in the generation of the six-membered structure with aromatic CC bonds, and (3) C³O breaking and C¹C⁵ formation that occur simultaneously to generate the keto-intermediate, which finally

produces *ortho*-substituted phenol. The present work will open a doorway to new non-thermal reactions induced by the molecular vibrational excitation in the electronic ground state.

Acknowledgments

The authors are grateful to the Information Technology Center of the University of Electro-Communications for their support of the DFT calculations.

Appendix A. Supplementary data

Supplementary data associated with this letter can be found, in the online version, at [doi:10.1016/j.cplett.2010.11.028](https://doi.org/10.1016/j.cplett.2010.11.028).

References

- [1] E. Bemberg, P. Luger, J. Membr. Biol. 11 (1973) 177.
- [2] J.T. Knudtson, E.M. Eyring, Annu. Rev. Phys. Chem. 25 (1974) 255.
- [3] W. Brock, G. Stark, P.S. Jordan, Biophys. Chem. 13 (1981) 329.
- [4] G. Stark, M. Strasle, Z. Takacz, J. Membr. Biol. 89 (1986) 23.
- [5] C.M. Phillips, Y. Mizutani, R.M. Hochstrasser, Proc. Natl. Acad. Sci. USA 92 (1995) 7292.
- [6] K. Yamamoto, Y. Mizutani, T. Kitagawa, Biophys. J. 79 (2000) 485.
- [7] T. Yatsuhashi, N. Nakashima, Bull. Chem. Soc. Jpn. 74 (2001) 579.
- [8] J. Kubelka, Photochem. Photobiol. Sci. 8 (2009) 499.
- [9] R. Gedye, F. Smith, K. Westaway, H. Ali, L. Baldisera, L. Laberge, J. Rousell, Tetrahedron Lett. 27 (1986) 279.
- [10] R.J. Giguere, T.L. Bray, S.M. Duncan, G. Majtich, Tetrahedron Lett. 27 (1986) 4945.
- [11] S. Caddick, Tetrahedron 51 (1995) 10403.
- [12] C.O. Kappe Angew. Chem. Int. Ed. 43 (2004) 6250.
- [13] S. Caddick, R. Fitzmaurice, Tetrahedron 65 (2009) 3325.
- [14] C.O. Kappe, D. Dallinger, Mol. Divers 13 (2009) 71.
- [15] S. Kikuchi, T. Tsubo, T. Ashizawa, T. Yamada Chem. Lett. 39 (2010) 574575.
- [16] A. Loupy (Ed.), Microwaves in Organic Synthesis, second Edn., Wiley-VCH, Weinheim, 2006.
- [17] I. Iwakura, A. Yabushita, T. Kobayashi, J. Am. Chem. Soc. 131 (2009) 688.
- [18] I. Iwakura, A. Yabushita, T. Kobayashi, Chem. Lett. 39 (2010) 374.
- [19] A. Baltuska, T. Fuji, T. Kobayashi, Opt. Lett. 27 (2002) 306.
- [20] L. Claisen, Chem. Ber. 45 (1912) 3157.
- [21] R. Hoffmann, R.B. Woodward, Acc. Chem. Res. 1 (1968) 17.
- [22] K. Fukui, Acc. Chem. Res. 4 (1971) 57.
- [23] M.S. Kharasch, G. Stampa, W. Nudenberg, Science 116 (1952) 309.
- [24] F. Galindo, J. Photochem. Photobiol. C: Photochem. Rev. 6 (2005) 123.
- [25] M.J.J. Vrakking, D.M. Villeneuve, A. Stolow, Phys. Rev. A 54 (1996) R37.
- [26] M.J. Frisch et al. Gaussian 03, Revision, D. 02, Gaussian, Wallingford CT, 2004.
- [27] T. Yagasaki, S. Saito, J. Chem. Phys. 128 (2008) 154521.
- [28] S. Yamabe, S. Okumoto, T. Hayashi, J. Org. Chem. 61 (1996) 6218.
- [29] B. Gmez, P.K. Chattaraj, E. Chamorro, R. Contreras, P. Fuentealba, J. Phys. Chem. A 106 (2002) 11227.
- [30] J.M. Jean, G.R. Fleming, J. Chem. Phys. 103 (1995) 2092.
- [31] F. Rosca, A.T.N. Kumar, X. Ye, T. Sjodin, A.A. Demidov, P.M. Champion, J. Phys. Chem. A 104 (2000) 4280.
- [32] A.T.N. Kumar, F. Rosca, A. Widom, P.M. Champion, J. Chem. Phys. 114 (2001) 701.