JOC *Note*

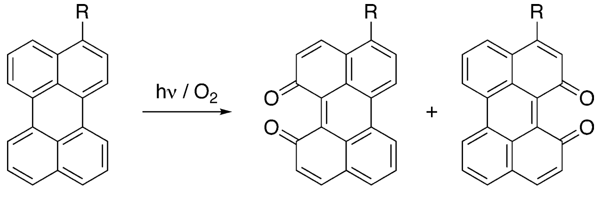
Photooxygenation of Alkynylperylenes. Formation of Dibenzo[*jk*,*mn*]phenanthrene-4,5-diones

Hajime Maeda,*,† Yasuaki Nanai,† Kazuhiko Mizuno,†
Junya Chiba,*,‡ Sakiko Takeshima,‡ and Masahiko Inouye‡

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan, and Graduate School of Pharmaceutical Sciences, University of Toyama, Sugitani 2630, Toyama 930-0194, Japan

maeda-h@chem.osakafu-u.ac.jp; chiba@pha.u-toyama.ac.jp

Received July 30, 2007



3-(1-Alkynyl)perylenes undergo oxygenation when subjected to irradiation with visible light under aerated conditions. The structures of novel oxygenated products formed in this manner are assigned as regioisomeric dibenzo[*jk*,*mn*]phenanthrene-4,5-diones.

Photooxygenation of organic molecules has been used in organic syntheses as a clean method to carry out oxygenation reactions as well in the low-temperature synthesis of unstable peroxides.[1] Many synthetic and mechanistic studies have been devoted to photooxygenations of alkenes, dienes, amines, aromatic compounds, and heterocycles which are promoted by photochemically generated singlet oxygen or electron-transfer sensitization. As for the photooxygenation of aromatic compounds, that of naphthalene[1a−c,2] and anthracene[1a−c,3] derivatives, leading to the formation of endoperoxides and dione products, has been extensively studied. Photooxygenation reactions involving the benzene ring are limited to electron-donating-substituted[4] and structurally strained benzene (e.g., cyclophanes) derivatives.[5] Photooxygenation of more condensed polycyclic aromatic hydrocarbons, such as naphthacene,[6] pentacene,[7] benzo[*a*]anthracene,[8] dibenzo[*a*,*j*]anthracene,[9] dibenzo[*a*,*o*]perylene,[10] dibenzo[*b*,*n*]perylene,[11] terrylene,[12] tetrabenzo[*a*,*c*,*l*,*n*]pentacene,[13] and diphenanthro[5,4,3-*abcd*:5′,4′,3′-*jklm*]perylene[14]

[†] Osaka Prefecture University.

[‡] University of Toyama.

(1) (a) Musgrave, O. C. *Chem. Rev.* **1969**, *69*, 499−531. (b) Adams, W. R. *Oxidation* **1971**, *2*, 65−112. (c) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133−336. (d) George, M. V.; Bhat, V. *Chem. Rev.* **1979**, *79*, 447−478. (e) Lopez, L. *Top. Curr. Chem.* **1990**, *156*, 117−166. (f) Jefford, C. W. *Chem. Soc. Rev.* **1993**, *22*, 59−66. (g) Tanielian, C.; Mechin, R.; Seghrouchni, R.; Schweitzer, C. *Photochem. Photobiol.* **2000**, *71*, 12−19. (h) Orfanopoulos, M. *Mol. Supramol. Photochem.* **2001**, *8*, 243−285. (i) Adam, W.; Bosio, S.; Bartoschek, A.; Griesbeck, A. G. *CRC Handb. Org. Photochem. Photobiol., 2nd ed.* **2004**, 25/1−25/19. (j) Iesce, M. R.; Cermola, F.; Temussi, F. *Curr. Org. Chem.* **2005**, *9*, 109−139. (k) Iesce, M. R. *Mol. Supramol. Photochem.* **2005**, *12*, 299−363. (l) Clennan, E. L. *Mol. Supramol. Photochem.* **2005**, *12*, 365−390. (m) Stratakis, M. *Curr. Org. Synth.* **2005**, *2*, 281−299. (n) Griesbeck, A. G.; El-Idreesy, T. T.; Bartoschek, A. *Pure Appl. Chem.* **2005**, *77*, 1059−1074. (o) Clennan, E. L.; Pace, A. *Tetrahedron* **2005**, *61*, 6665−6691.

(2) (a) Jefford, C. W.; Jaggi, D.; Boukouvalas, J.; Kohmoto, S. *J. Am. Chem. Soc.* **1983**, *105*, 6497−6498. (b) Santamaria, J.; Gabillet, P.; Bokobza, E. L. *Tetrahedron Lett.* **1984**, *25*, 2139−2142. (c) Bokobza, L.; Santamaria, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 269−271. (d) Jefford, C. W.; Favarger, F.; Ferro, S.; Chambaz, D.; Bringhen, A.; Bernardinelli, G.; Boukouvalas, J. *Helv. Chim. Acta* **1986**, *69*, 1778−1786. (e) Aubry, J. M.; Cazin, B.; Duprat, F. *J. Org. Chem.* **1989**, *54*, 726−728. (f) Adam, W.; Prein, M. *J. Am. Chem. Soc.* **1993**, *115*, 3766−3767. (g) Adam, W.; Prein, M. *Tetrahedron Lett.* **1994**, *35*, 4331−4334. (h) Wasserman, H. H.; Wiberg, K. B.; Larsen, D. L.; Parr, J. *J. Org. Chem.* **2005**, *70*, 105−109.

(3) (a) Rigaudy, J.; Scribe, P.; Brelière, C. *Tetrahedron* **1981**, *37*, 2585−2593. (b) Santamaria, J. *Tetrahedron Lett.* **1981**, *22*, 4511−4514. (c) Keana, J. F. W.; Prabhu, V. S.; Ohmiya, S.; Klopfenstein, C. E. *J. Org. Chem.* **1986**, *51*, 3456−3462. (d) Meador, M. A.; Hart, H. *J. Org. Chem.* **1989**, *54*, 2336−2341. (e) Rak, S. F.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1990**, *55*, 4794−4801. (f) Sigman, M. E.; Zingg, S. P.; Pagni, R. M.; Burns, J. H. *Tetrahedron Lett.* **1991**, *32*, 5737−5740. (g) Motoyoshiya, J.; Masunaga, T.; Harumoto, D.; Ishiguro, S.; Narita, S.; Hayashi, S. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 1166−1171. (h) Kotera, M.; Lehn, J.-M.; Vigneron, J.-P. *Tetrahedron* **1995**, *51*, 1953−1972. (i) Nardello, V.; Aubry, J.-M. *Tetrahedron Lett.* **1997**, *38*, 7361−7364. (j) Trabanco, A. A.; Montalban, A. G.; Rumbles, G.; Barrett, A. G. M.; Hoffman, B. M. *Synlett* **2000**, 1010−1012. (k) Catir, M.; Kilic, H. *Synlett* **2003**, 1180−1182. (l) Donkers, R. L.; Workentin, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 1688−1698. (m) Kuroda, S.; Oda, M.; Syumiya, H.; Shaheen, S. M. I.; Miyatake, R.; Nishikawa, T.; Yoneda, A.; Tanaka, T.; Mouri, M.; Kyogoku, M. *Heterocycles* **2004**, *62*, 153−159. (n) Kotani, H.; Ohkubo, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2004**, *126*, 15999−16006. (o) Nardello, V.; Aubry, J.-M.; Johnston, P.; Bulduk, I.; de Vries, A. H. M.; Alsters, P. L. *Synlett* **2005**, 2667−2669. (p) Song, B.; Wang, G.; Tan, M.; Yuan, J. *New J. Chem.* **2005**, *29*, 1431−1438. (q) Fuchter, M. J.; Hoffman, B. M.; Barrett, A. G. M. *J. Org. Chem.* **2006**, *71*, 724−729.

(4) (a) Saito, I.; Tamoto, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2889−2892. (b) Santamaria, J.; Rigaudy, J. *Tetrahedron* **1980**, *36*, 2453−2457. (c) Liang, J.-J.; Foote, C. S. *Tetrahedron Lett.* **1982**, *23*, 3039−3042. (d) Zadok, E.; Rubinraut, S.; Frolow, F.; Mazur, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2489−2494. (e) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Tetrahedron Lett.* **1985**, *26*, 5823−5826. (f) Tamai, T.; Mizuno, K.; Hashida, I.; Otsuji, Y. *Photochem. Photobiol.* **1991**, *54*, 23−29.

(5) (a) Gray, R.; Boekelheide, V. *J. Am. Chem. Soc.* **1979**, *101*, 2128−2136. (b) Stöbbe, M.; Kirchmeyer, S.; Adiwidjaja, G.; De Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 171−173. (c) Wijsman, G. W.; van Es, D. S.; de Wolf, W. H.; Bickelhaupt, F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 726−728. (d) Sawada, T.; Mimura, K.; Thiemann, T.; Yamato, T.; Tashiro, M.; Mataka, S. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1369−1371.

(6) (a) Dufraisse, C.; Horclois, R. *Bull. Soc. Chim. Fr.* **1936**, 1880−1893. (b) Dufraisse, C.; Horclois, R. *Bull. Soc. Chim. Fr.* **1936**, 1894−1905. (c) Rigaudy, J.; Sparfel, D. *Bull. Soc. Chim. Fr.* **1977**, Pt. 2, 742−748. (d) Sy, A.; Hart, H. *J. Org. Chem.* **1979**, *44*, 7−9. (e) Caminade, A. M.; Khatib, F. E.; Koenig, M.; Aubry, J. M. *Can. J. Chem.* **1985**, *63*, 3203−3209. (f) Dabestani, R.; Nelson, M.; Sigman, M. E. *Photochem. Photobiol.* **1996**, *64*, 80−86. (g) Aubry, J.-M.; Bouttemy, S. *J. Am. Chem. Soc.* **1997**, *119*, 5286−5294. (h) Pierlot, C.; Nardello, V.; Schrive, J.; Mabille, C.; Barbillat, J.; Sombret, B.; Aubry, J.-M. *J. Org. Chem.* **2002**, *67*, 2418−2423. (i) Harrington, L. E.; Britten, J. F.; McGlinchey, M. J. *Org. Lett.* **2004**, *6*, 787−790.

(7) (a) Sparfel, D.; Gobert, F.; Rigaudy, J. *Tetrahedron* **1980**, *36*, 2225−2235. (b) Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410−411. (c) Chan, S. H.; Lee, H. K.; Wang, Y. M.; Fu, N. Y.; Chen, X. M.; Cai, Z. W.; Wong, H. N. C. *Chem. Commun.* **2005**, 66−68. (d) Uno, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Yamada, H.; Okujima, T.; Ogawa, T.; Ono, N. *Tetrahedron Lett.* **2005**, *46*, 1981−1983.

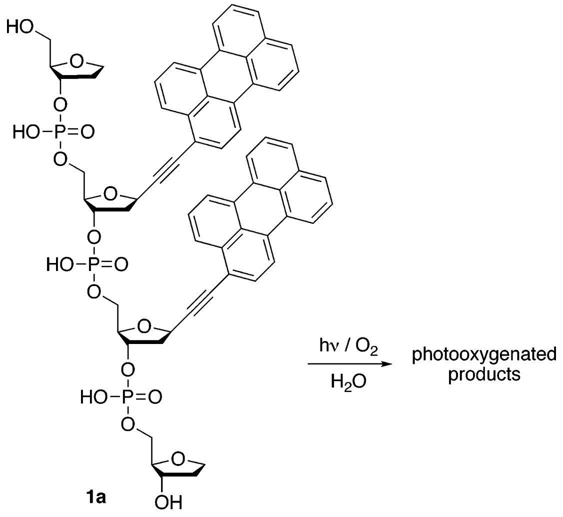
(8) (a) Newman, M. S.; Khanna, J. M. *J. Org. Chem.* **1979**, *44*, 866−868. (b) Lee, H.; Harvey, R. G. *J. Org. Chem.* **1986**, *51*, 3502−3507.

(9) Noller, K.; Kosteyn, F.; Meier, H. *Chem. Ber.* **1988**, *121*, 1609−1615.

(10) (a) Brockmann, H.; Mühlmann, R. *Chem. Ber.* **1948**, *81*, 467−472. (b) Brockmann, H.; Dicke, F. *Chem. Ber.* **1970**, *103*, 7−16. (c) Seip, M.; Brauer, H.-D. *J. Am. Chem. Soc.* **1992**, *114*, 4486−4490.

10.1021/jo7016668 CCC: $37.00

SCHEME 1. Photooxygenation of DNA-like Fluorescent Perylene Dimer Based on Alkynyl *C*-Nucleoside



derivatives has also been explored. Since more condensed polyaromatic compounds have low triplet energies, they can serve to sensitize singlet oxygen generation without the need for external photosensitizers.

Photooxygenation of perylene, a versatile visible-light absorbing fluorophore, has not been fully probed. To the best of our knowledge, the sole reported study was carried out by Guillet et al., where perylene was photooxygenated in water in the presence of a water-soluble polymer photosensitizer.[15] Importantly, photooxygenation reactions of substituted perylenes have not been described.

Recently, we described the synthesis of DNA-like fluorescent oligomers composed of alkynyl *β*-D-ribofuranosides bearing pyrene, perylene, and anthracene fluorophores, and reported their homo- and heteroexcimer emissions.[16] During the course of that study, we noticed that the alkynylperylene dimer **1a** undergoes facile photobleaching upon exposure to visible light. Below, we report the novel photooxygenation reaction of alkynylperylenes that is responsible for photobleaching and alert photochemists that the fluorescence intensity of perylene is easily decreased owing to this process.

When the photophysical properties of nucleosides bearing fluorophores were investigated in aerated water, we became aware of the instability of **1a** when exposed to ambient indoor lighting (Scheme 1). The fluorescence spectrum of pure **1a** contains a typical intramolecular excimer emission around 600 nm.[16] In Figure 1 is shown the time-dependency of the fluorescence spectrum of **1a** in aerated water upon irradiation with a desktop fluorescent lamp. Upon irradiation, the emission due to the perylene excimer decreases concurrently with an increase of monomer emission with an isoemissive point. Monomer emission reaches a maximum after 30 h of irradiation and then begins to decay. These observations indicate that at first one of the two perylene fluorophores in **1a** is converted to a nonfluorescent moiety and then the other perylene group is transformed to a nonfluorescent moiety. HPLC separation and MALDI-TOF mass analysis of the crude mixture obtained after 24 h of irradiation of **1a** indicates that products having molecular weights that correspond to adducts of one and two molecules of dioxygen are produced (Figure S3, Supporting Information).

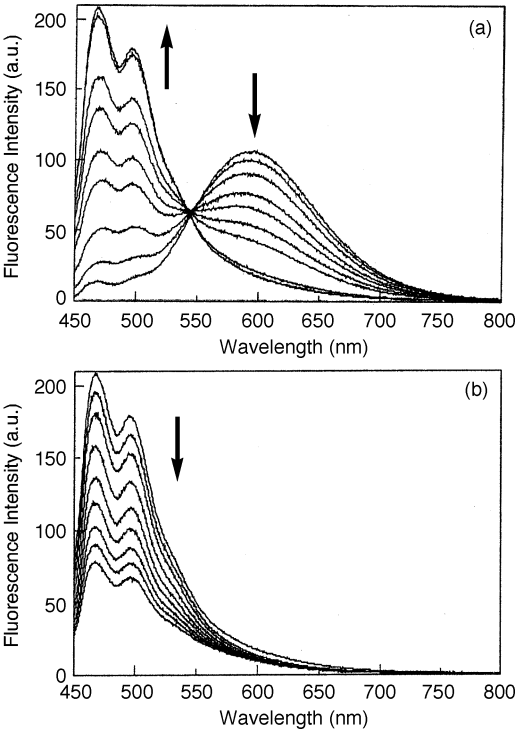


FIGURE 1. Time-dependency of fluorescence spectra of **1a** upon (a) 0−30 and (b) 30−201 h of photoirradiation.

Stimulated by this observation, we carried out the photoreaction of readily available alkynylperylenes and determined the structures of the oxygenated products. A chloroform solution of 3-(1-hexynyl)perylene **1b** (10 mM, 200 mL) was irradiated by using an incandescent lamp (300 W) with continuous stirring and bubbling of dioxygen at room temperature for 24 h (Scheme 2). TLC analysis showed that components having higher polarities (R_f 0.2, $CHCl_3$) than the substrate were observed in the crude photolysate. Silica gel column chromatography and preparative HPLC led to isolation of a 1:1 regioisomeric mixture of photooxygenated products as an orange solid in a 10% yield (Table 1, run 2). One regioisomer was isolated by continuous preparative HPLC.

The structures of products were assigned as dibenzo[*jk*,*mn*]-phenanthrene-4,5-diones **2b** and **3b** (Scheme 2) by using ^{1}H NMR, ^{1}H−^{1}H COSY, ^{13}C NMR, ESI-MS, HRMS, and IR. The ^{1}H−^{1}H COSY spectrum of **2b** is shown in Figure 2. As expected from the structure of **2b**, its 1D ^{1}H NMR spectrum contains three pairs of doublets which are coupled to each other (H1−

---

[11] (a) Hewgill, F. R.; Stewart, J. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1305−1311. (b) Benshafrut, R.; Hoffman, R. E.; Rabinovitz, M.; Müllen, K. *J. Org. Chem.* **1999**, *64*, 644−647.

[12] Christ, T.; Kulzer, F.; Bordat, P.; Basché, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 4192−4195.

[13] Schuster, I. I.; Craciun, L.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron* **2002**, *58*, 8875−8882.

[14] (a) Broene, R. D.; Diederich, F. *Tetrahedron Lett.* **1991**, *32*, 5227−5230. (b) Sakai, K.; Nagashima, U.; Fujisawa, S.; Uchida, A.; Ohshima, S.; Oonishi, I. *Chem. Lett.* **1993**, 577−580. (c) Ohshima, S.; Uchida, A.; Horiguchi, S.; Suzuki, A.; Fujisawa, S.; Oonishi, I. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 924−928.

[15] (a) White, B.; Nowakowska, M.; Guillet, J. E. *J. Photochem. Photobiol. A*: *Chem.* **1989**, *50*, 147−156. (b) Burke, N. A. D.; Templin, M.; Guillet, J. E. *J. Photochem. Photobiol. A*: *Chem.* **1996**, *100*, 93−100. See also refs 11b and: (c) Zinke, A.; Unterkreuter, E. *Monatshefte* **1919**, *40*, 405−410. (d) Nowakowska, M.; Guillet, J. E. *Chem. Br.* **1991**, *27*, 327−330.

[16] Chiba, J.; Takeshima, S.; Mishima, K.; Maeda, H.; Nanai, Y.; Mizuno, K.; Inouye, M. *Chem. Eur. J.* **2007**, *13*, 8124−8130.

SCHEME 2. Photooxygenation of Perylene Derivatives

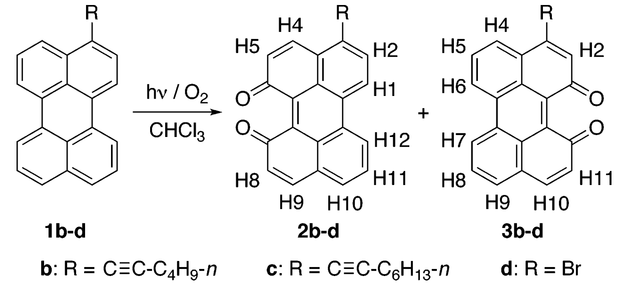


TABLE 1. Photooxygenation of Perylene Derivatives

run no.	sub-strate	lamp	irradiation time (h)	additive	yields (%) 2	yields (%) 3
1[a]	**1a**	desktop fluorescent lamp (>400 nm)	201	none	b	b
2[c]	**1b**	incandescent lamp (>400 nm)	24	none	5	5
3[c]	**1b**	high-pressure Hg lamp (>280 nm)	24	none	0	0
4[c]	**1c**	photoflood lamp (>400 nm)	72	none	6[d,e]	
5[c]	**1d**	Xe lamp, O-58 filter (>580 nm)	48	methylene blue	9[d]	

[a] In water. [b] Not determined. See Figure 1. [c] In CHCl$_3$. [d] Mixture of **2** and **3**. [e] Major isomer was **2c**.

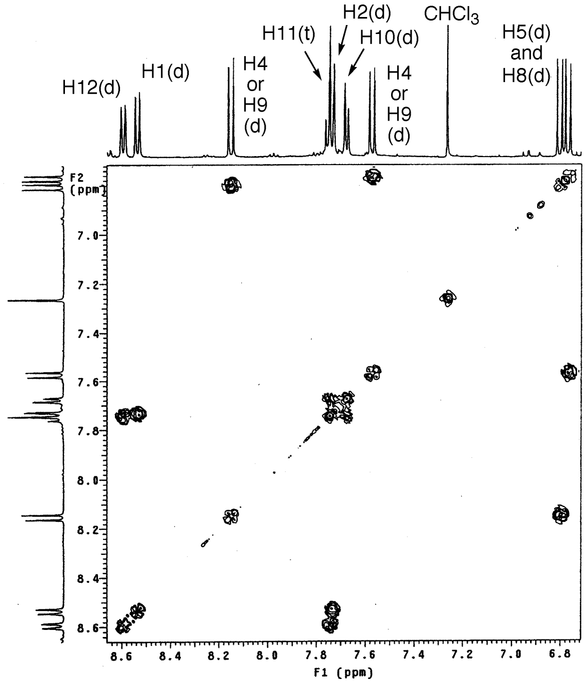


FIGURE 2. ^{1}H−^{1}H COSY spectrum of **2b**.

H2, H4−H5, and H8−H9) and one doublet−triplet−doublet sequence (H10−H11−H12). All signals observed in the COSY spectrum agree with these coupling patterns. The structure of **3b** was assigned by comparing the spectral data of the mixture of regioisomers to that of **2b** (Figures S7 and S8, Supporting Information). The ^{1}H NMR spectrum of **3b**, containing a singlet (H2, 6.95 ppm) and two triplets (H5 and H8, 7.80 and 7.86 ppm), is in accord with its structure. The ^{13}C NMR spectrum of **2b** shows overlapped carbonyl signals at 187.4 ppm and its IR spectrum contains two carbonyl stretching bands at 1657 and 1625 cm^{-1}. Finally, MNa$^+$ (385) and MH$^+$ (363) fragments are observed in ESI-MS of **2b**.

Photoreaction of 3-(1-octynyl)perylene **1c** under similar conditions also proceeds in an analogous manner (run 4). The absorption bands of perylene derivatives extend into the visible region. For example, **1b** in cyclohexane has maxima at 455 ($\epsilon = 4.71 \times 10^4$ mol^{-1} dm^3 cm^{-1}), 426 ($\epsilon = 3.47 \times 10^4$ mol^{-1} dm^3 cm^{-1}), and 403 nm ($\epsilon = 1.54 \times 10^4$ mol^{-1} dm^3 cm^{-1}). Consequently, the irradiation by using an incandescent lamp or a photoflood lamp is more effective for promoting photooxygenation than that by using a high-pressure mercury lamp (Table 1, run 3).

To the best of our knowledge, the observations reported above represent a rare case in which simple aromatic compounds readily undergo photooxygenated in the absence of a singlet oxygen generator or electron-transfer catalyst. Two possible mechanisms for the novel photooxygenation reaction are shown in Scheme 3. One involves the generation of ^{1}O$_2$ by a route that begins with the singlet excited state of alkynylperylene (^{1}**1***), formed by photoexcitation of **1**. Intersystem crossing (ISC) forms the excited triplet state (^{3}**1***)[17] and then energy transfer from ^{3}**1*** to ground state dioxygen (^{3}O$_2$) takes place to generate ^{1}O$_2$.[18] The second possible mechanism involves single electron transfer via contact charge transfer (CT) complex[19] formed from **1** and ^{3}O$_2$. The endoperoxides **4** and **5** produced through these pathways undergo oxidative cleavage to give oxygenated products **2** and **3**.

To gain insight into which of the above mechanisms operates in the oxygenation process, reaction of ^{1}O$_2$ with **1b** was investigated. When photoreactions of **1b** were carried out in the presence of dyes, such as tetraphenylporphyrin, methylene blue, and rose bengal, as ^{1}O$_2$ generators, product yields were unchanged. Moreover, photooxygenation of **1b** did not occur in the presence of the ^{1}O$_2$ quencher 1,4-diazabicyclo[2.2.2]-octane (DABCO) and **1b** was recovered quantitatively. Photoreaction of 3-bromoperylene (**1d**) in the presence of methylene blue, promoted by irradiation with a Xe lamp equipped with O-58 filter (>580 nm, conditions under which only sensitizer absorbs the light) gave **2d** and **3d** in moderate yields (Table 1, run 5). This result is likely due to enhanced ISC rate caused by a heavy atom effect. Absorption spectra, obtained on argon-purged and dioxygen-purged solutions of **1b** showed that a several nanometer shift occurs in the case of dioxygen-purged solution. To get information about the electron-transfer mechanism the effects of Mg(ClO$_4$)$_2$ as a promoter of charge separation[4e,f,20] and polar solvents such as acetonitrile were investigated. In each case no changes in reaction yields were noted. Under dark condition, the photooxygenated products were

---

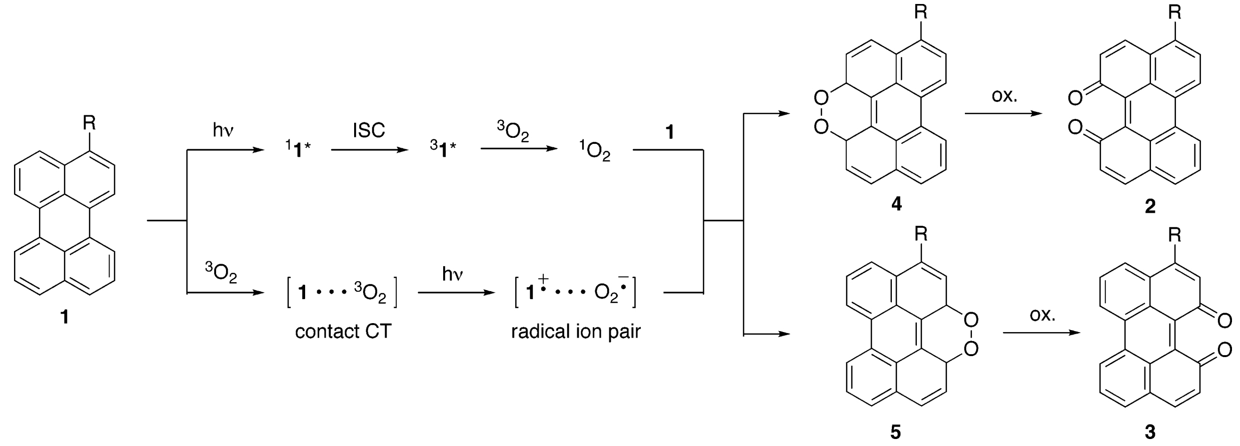
[17] (a) Parker, C. A.; Joyce, T. A. *Chem. Commun.* **1966**, 108−109. (b) Nakabayashi, K.; Toki, S.; Takamuku, S. *Chem. Lett.* **1986**, 1889−1892.

[18] McLean, A. J.; McGarvey, D. J.; Truscott, G.; Lambert, C. R.; Land, E. J. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3075−3080.

[19] (a) Dharamsi, A. N.; Tulip, J. *Chem. Phys. Lett.* **1980**, *71*, 224−227. (b) Kojima, M.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3863−3868. (c) Logunov, S. L.; Rodgers, M. A. J. *J. Phys. Chem.* **1993**, *97*, 5643−5648. (d) Kuriyama, Y.; Ogilby, P. R.; Mikkelsen, K. V. *J. Phys. Chem.* **1994**, *98*, 11918−11923.

[20] (a) Loupy, A.; Tchoubar, B.; Astruc, D. *Chem. Rev.* **1992**, *92*, 1141−1165. (b) Mizuno, K.; Otsuji, Y. *Top. Curr. Chem.* **1994**, *169*, 301−346. (c) Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1−28. (d) Maeda, H.; Nakagawa, H.; Mizuno, K. *Photochem. Photobiol. Sci.* **2003**, *2*, 1056−1058. (e) Maeda, H.; Miyamoto, H.; Mizuno, K. *Chem. Lett.* **2004**, *33*, 462−463.

SCHEME 3. Mechanism for the Photooxygenation



not obtained. Photoreaction of perylene did not proceed under the conditions used for reaction of **1a**−**d**.

The above results suggest that the mechanism involving $^1O_2$ is more likely for the photooxygenation reaction. The reason for the large difference in efficiency of the reaction between **1a** and **1b**−**d** is likely due to the fact that photooxygenation via a perylene excimer is faster than that via a perylene monomer. However, due to the low solubility of perylene derivatives in organic solvents and water, attachment of the two perylene core onto a water-soluble chain (**1a**) or putting it into a hydrophilic environment by mixing with a water-soluble polymer[15a,b] is required to have a sufficient concentration of the more reactive perylene excimer. In addition, the alkynyl groups might contribute by increasing solubility and lowering triplet energy.

In summary, we have observed an unprecedented photooxygenation reaction of alkynylperylenes. This is the first example of photooxygenation of substituted perylenes. Recently, much attention has been focused on the attachment of perylene fluorophore to nucleosides.[21] However, the results presented above suggest that attention must be paid to the inevitable oxygenation of the perylene fluorophore when it is present in such biomolecules.

Experimental Section

Photooxygenation of 1a. A solution of **1a** in MilliQ water (1×10^{-5} M) in a 1 cm × 1 cm quartz cell was irradiated by using a desktop fluorescent lamp without stirring at room temperature. Progress of the reaction was monitored by fluorescence spectroscopy (Figure 1).

Photooxygenation of 3-(1-Hexynyl)perylene (1b). A chloroform solution of 3-(1-hexynyl)perylene **1b** (10 mM, 200 mL) was irradiated by using an incandescent lamp with continuous bubbling of dioxygen for 24 h at room temperature. Components with higher polarity than **1b** were observed by TLC analysis ($CHCl_3$, R_f 0.2). Silica gel column chromatography and HPLC gave an orange solid containing **2b** and **3b** in total 10% yield. One regioisomer (**2b**) could be isolated by continuously cutting off the shoulder of the peak in recycling preparative HPLC.

Data for 2b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.02 (t, $J = 7.48$ Hz, 3 H), 1.57 (sextet, $J = 7.55$ Hz, 2 H), 1.72 (quint, $J = 7.48$ Hz, 2 H), 2.60 (t, $J = 7.26$ Hz, 2 H), 6.77 (d, $J = 9.83$ Hz, 1 H), 6.81 (d, $J = 10.25$ Hz, 1 H), 7.57 (d, $J = 9.83$ Hz, 1 H), 7.68 (d, $J = 7.26$ Hz, 1 H), 7.74 (d, $J = 8.54$ Hz, 1 H), 7.74 (t, $J = 8.55$ Hz, 1 H), 8.15 (d, $J = 9.83$ Hz, 1 H), 8.54 (d, $J = 8.97$ Hz, 1 H), 8.59 (d, $J = 8.54$ Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.9, 17.1, 19.8, 22.4, 78.2, 100.8, 124.7, 125.3, 125.6, 127.2, 127.3, 129.5, 129.96, 130.04, 130.4, 130.5, 130.59, 130.63, 130.8, 132.9, 134.8, 135.7, 138.8, 140.7, 187.4; IR (KBr) 1625 (C=O), 1657 (C=O), 2219 (C≡C) cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{18}NaO_2$ 385.1205, found 385.1197.

Acknowledgment. The present work is supported by the Grant-in-Aid for Scientific Research (KAKENHI) in Priority Area “Molecular Nano Dynamics” (17034056) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

Supporting Information Available: Experimental details for the syntheses and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO7016668

---

[21] (a) Gao, J.; Strässler, C.; Tahmassebi, D.; Kool, E. T. *J. Am. Chem. Soc.* **2002**, *124*, 11590−11591. (b) Gao, J.; Watanabe, S.; Kool, E. T. *J. Am. Chem. Soc.* **2004**, *126*, 12748−12749. (c) Skorobogatyi, M. V.; Malakhov, A. D.; Pchelintseva, A. A.; Turban, A. A.; Bondarev, S. L.; Korshun, V. A. *ChemBioChem.* **2006**, *7*, 810−816.