

Photooxygenation Product of Dibenzo[*a,j*]perylene

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The photooxygenation of dibenzo[*a,j*]perylene by visible light irradiation was studied spectroscopically. The structure of unstable photooxygenation product was deduced from spectroscopic data and results of MO calculations to be as 8,12b-endoperoxide of dibenzo[*a,j*]perylene. This endoperoxide released oxygen gradually at room temperature, recovering the original hydrocarbon. The activation energy for this dark reaction was determined to be 21.4 ± 0.5 kcal/mol in benzene and 22.6 ± 0.5 kcal/mol in ethanol.

Reactions of excited aromatic hydrocarbons with molecular oxygen have been extensively studied in relation to the properties of singlet oxygen and quenching of excited singlet or triplet states.¹⁾ However, the mode of reaction is by no means simple and investigations have been concentrated on rather small molecules as anthracene and 9,10-diphenylanthracene. Rubrene may be the only medium size aromatic hydrocarbon which received detailed and sufficiently unambiguous investigations.²⁾ Helianthrene (dibenzo[*a,o*]perylene) and its derivatives have also attracted the interest of several authors but the structures of their photooxygenation products have yet to be determined by further investigations.²⁾

In the course of the syntheses and the study of photoconductive properties of aromatic hydrocarbons,³⁾ we observed that dibenzo[*a,j*]perylene, a structural isomer of helianthrene, underwent a typical photochemical reaction in organic solvents like benzene and ethanol. This phenomenon had already been reported by Clar⁴⁾ and could be interpreted as photooxygenation reaction like those of helianthrene and its derivatives. We have further investigated this reaction and the properties of the rather unstable oxygenation product because Clar's report was not much more than mere observation and also because photooxygenation process might possibly be related to the photoconductive properties of evaporated thin films or crystals of similar aromatic hydrocarbons.

Experimental

Synthesis of Dibenzo[*a,j*]perylene. Dibenzo[*a,j*]perylene was synthesized by almost the same method as Clar's.⁴⁾ 1-Chloroanthrone (mp 138 °C) was boiled and stirred with zinc chloride in pyridine at 200 °C for 20 h. Then it was treated with sodium dithionite to give dibenzo[*a,j*]perylene-3,9-dione. The dibenzoperylenequinone was boiled with zinc dust in pyridine, and glacial acetic acid was gradually added to the solution, which was then boiled and stirred for 5 h. From the reaction product, dibenzo[*a,j*]perylene was extracted with benzene and was purified by column chromatography with activated alumina. Further purification was carried out by high vacuum sublimation.

Photooxygenation and Related Measurements. Benzene or ethanol solution of dibenzo[*a,j*]perylene in 1 cm rectangular silica cell was irradiated by a 30 W tungsten lamp through a sharp cut off filter, Toshiba VY-50, transparent only for wavelength longer than 500 nm. The spectral change induced by the irradiation was observed with a Shimadzu UV-210 spectrophotometer.

The rate of thermal detachment of oxygen from the photooxygenation product was also observed by the same spectrophotometer, while the temperature of the sample solution was controlled to within ± 0.5 °C by a specially designed bronze cell holder and a thermister temperature controller. Benzene and ethanol were used as solvents and temperature was controlled at several points between 40 °C and 75 °C.

The ESR spectrum of *ca.* 10^{-5} mol/l benzene solution of dibenzoperylene⁵⁾ was measured with ESR spectrometer NIHON DENSHI JES-PE-3X, before and after visible light irradiation under air pressure of about 0.1 Pa and 100 kPa.

A preliminary measurement of the overall efficiency of the photooxygenation reaction was also performed as follows. Benzene solution of dibenzo[*a,j*]perylene in a 1 cm rectangular silica cell was irradiated with the 556 nm monochromatic light, and the decrease of the hydrocarbon was monitored by the optical density change at 556 nm. The photon flux of the impinging light was measured making use of potassium tris(oxalato)ferrate(III) actinometer.

It has also been ascertained that singlet molecular oxygen reacts with dibenzo[*a,j*]perylene in its ground state to give the same oxygenation product as that obtained by photooxygenation. The singlet molecular oxygen was produced by adding NaOCl (*ca.* 5% commercial antiseptic solution PURELOX) onto H₂O₂ (35%, Koso Chemical Ltd.), and was immediately introduced, bubbling, into benzene solution of the hydrocarbon, which had previously been placed upon 30% H₂O₂.⁶⁾ The concentration of the benzene solution was about 10^{-5} mol/l and its spectra were measured before and after reaction and compared to each other.

Benzene and ethanol were reagent grade and were used without further purification.

Results and Discussion

Benzene or ethanol solution of dibenzo[*a,j*]perylene had been pink color but it changed to brownish color upon irradiation by room light. When the brownish solution was left in the dark at room temperature for a few days, the original color recovered. This phenomenon, which might be said a kind of photo- and thermo-chromism, could be repeated several times, although some percentage of dibenzo[*a,j*]perylene suffered permanent destruction due to some unknown side-reaction.

The absorption spectra of dibenzo[*a,j*]perylene in benzene are shown in Fig. 1. A strong absorption band with a typical vibrational structure is observed in the region between 450 and 600 nm. The region around 330—430 nm (especially 340—390 nm) seemed to be overlapped by some impurity absorption and

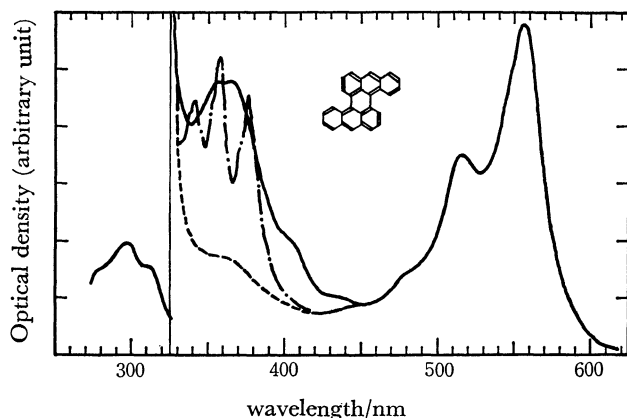


Fig. 1. Absorption spectra of dibenzo[*a,j*]perylene in benzene.

— and ----: Uncorrected spectra of two samples obtained by different purification procedures, - · - ·: corrected spectra.

was different from sample to sample. Repeated purification procedures by column chromatography and high vacuum sublimation could not eliminate completely the impurities responsible to those absorption. The fluorescence excitation spectra of very dilute benzene solution (*ca.* 10^{-7} mol/l) monitored by the fluorescence band shown in Fig. 4 under anaerobic conditions showed a broad and rather weak absorption band around 370 nm. This excitation spectra should resemble to the true absorption spectra. Taking also account of the spectral change during photochemical reaction, which will be described later, we deduced the true spectral shape in this region and showed it in Fig. 1.[†] Fortunately, there was only little change in this region of spectra during the photooxygenation and thermal deoxygenations. Therefore, we are free from complications due to these impurities in the present study.

When irradiated by a tungsten lamp through a sharp cut off filter, Toshiba VY-50, the spectra of ethanol solution changed as shown in Fig. 2. We could observe an isosbestic point near 455 nm. It is also illustrated in this figure that the solution regained about 85% intensity of original spectra after keeping it about a day in the dark at room temperature. We could observe the same spectral change also for benzene solution. A small deviation of the recovered spectra from the isosbestic point indicates that a small fraction

[†] The spectrum of helianthrene reported by Clar (p. 49, Ref. 5) was quite similar to that of our dibenzo[*a,j*]perylene, which implied that we synthesized helianthrene instead of dibenzo[*a,j*]perylene through some error. Brockmann and Mühlmann have reported different absorption maxima of helianthrene,⁷⁾ but they didn't give the whole spectra. We ascertained that our hydrocarbon could not be helianthrene because the intermediate quinone, which we used for dibenzo[*a,j*]perylene synthesis, did not give bisanthene-3,10-dione by photochemical reaction in pyridine under anaerobic condition. Helianthrene quinone, which is an inevitable intermediate for helianthrene synthesis, should give bisanthene-3,10-dione by such a reaction.⁸⁾

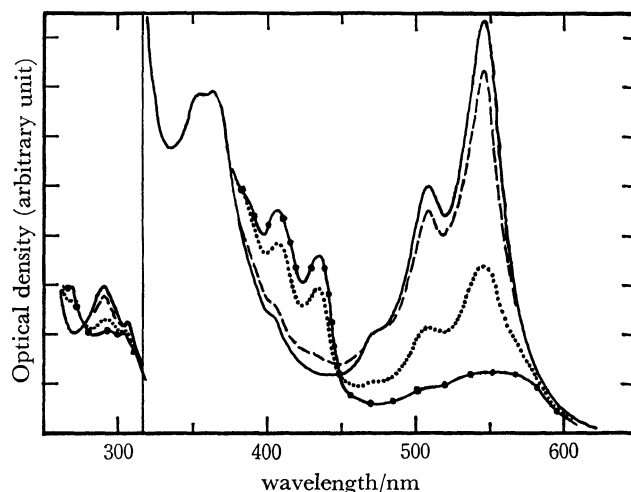


Fig. 2. Change of absorption spectra by visible light irradiation in ethanol.

—: Before irradiation, ·····: after 12 minutes irradiation, ———: after 50 minutes irradiation, - - - -: left in the dark at room temperature for a day after 50 minutes irradiation.

of dibenzo[*a,j*]perylene was permanently destroyed. By a careful treatment up to 95% intensity could be recovered both in benzene and ethanol. The spectral change above mentioned did not occur when the solution was evacuated to about 0.1 Pa as was expected.

The following two types of reaction paths can be proposed for this type of photooxygenation reaction.

- (1) $A(\text{Ground}) + h\nu \longrightarrow A^*(\text{Singlet})$
 $A^*(S) \longrightarrow A^*(\text{Triplet})$
 $A^*(T) + O_2(G, {}^3\Sigma_g^-) \longrightarrow AO_2$
- (2) $A(G) + h\nu \longrightarrow A^*(S)$
 $A^*(S) \longrightarrow A^*(T)$
 $A^*(T) + O_2(G, {}^3\Sigma_g^-) \longrightarrow A(G) + O_2(S, {}^1\Delta_g)$
 $A(G) + O_2(S, {}^1\Delta_g) \xrightarrow{k} AO_2$

We could observe that the rate of photobleaching of dibenzo[*a,j*]perylene was much faster in CCl_4 than in benzene. Because it has been reported that the lifetime of ${}^1\Delta_g O_2$ in CCl_4 is 700 μs , and is much longer than in benzene (lifetime 24 μs),⁹⁾ this observation suggests the participation of singlet oxygen. Furthermore, a similar spectral change was observed, when the benzene solution of dibenzo[*a,j*]perylene was treated under dark with singlet molecular oxygen as has been described in the experimental section. It should be also mentioned that $A(\text{Ground}) + O_2({}^1\Delta_g)$ correlates with the ground state of the product AO_2 exothermically and $A^*(T) + O_2(G, {}^3\Sigma_g^-)$ can only correlate with the excited state of AO_2 endothermically¹⁰⁾ (see Fig. 6). These observations and consideration lead to the conclusion that the type (2) is the appropriate reaction. Also it is reasonable to assign the new band between 370 and 450 nm to some sort of endoperoxide as is usually obtained or assumed in cases of similar reactions of other aromatic hydrocarbons.^{2,4)} We can assume several possible structures for the endoperoxide as shown in Fig. 3.

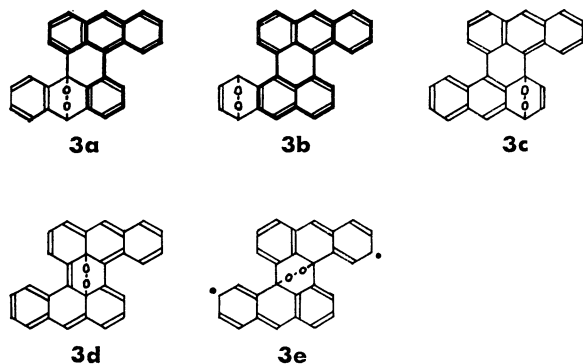


Fig. 3. Possible structures of photooxygenation products of dibenzo[*a,j*]perylene.

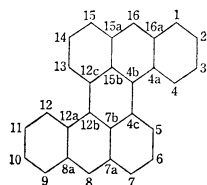
a: 9-Phenylanthracene type structure (8,12b-endoperoxide), **b:** benzo[*a*]perylene type structure (9,12-endoperoxide).

A biradical form similar to the structure **3e** in Fig. 3 was proposed for the thermochromic form of $A^{10,10'}$ -bianthrone by Woodward and Wasserman.¹¹⁾ We performed ESR measurement as described before but it didn't show any increase of ESR signal that could be attributed to the formation of any kind of biradical endoperoxide. Thus we can disregard the structure **3e**.

In order to select the most probable structure out of **3a**–**3d**, we carried out MO calculations. Table 1 shows the calculated self-polarizabilities for all carbon sites of dibenzo[*a,j*]perylene.

In view of the structures of similar hydrocarbons, tetrabenzo[*a,cd,j,lm*]perylene¹²⁾ and dibenzo[*jk,uv*]-dinaphtho[2,1,8,7-*defg*: 2',1',8',7'-*opqr*]pentacene,¹³⁾ dibenzo[*a,j*]perylene must have a non-planar structure due to the steric hindrances of two pairs of hydrogen

TABLE 1. SELF-POLARIZABILITIES ($\pi\pi$) OF DIBENZO[*a,j*]PERYLENE



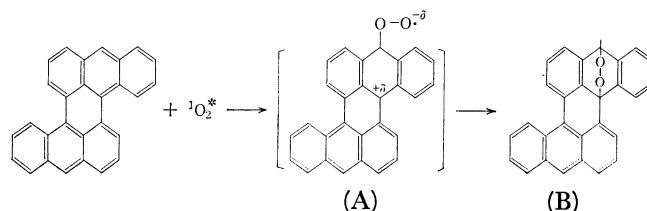
Position	$\pi\pi$	Fr	Position	$\pi\pi$	Fr
1, 9	0.461	0.462	4c, 12c	0.355	0.140
2, 10	0.406	0.405	5, 13	0.491	0.473
3, 11	0.421	0.415	6, 14	0.400	0.397
4, 12	0.438	0.446	7, 15	0.509	0.484
4a, 12a	0.355	0.143	7a, 15a	0.330	0.102
4b, 12b	0.395	0.188	8, 16	0.604	0.544
7b, 15b	0.354	0.152	8a, 16a	0.329	0.102

Pair positions	Sum of $\pi\pi$'s	Corresponding endoperoxide in Fig. 3
8+12b(16+4b)	0.999	3a
1+4(9+12)	0.899	3b
7+4c(15+12c)	0.864	3c
7b+15b	0.708	3d

atoms, the mean angle between two anthracene skeleton planes being about 30° (see Fig. 6a). However, we assumed a planar structure for the present MO calculations to avoid less important but cumbersome problems. Since the qualitative or semiquantitative features of π -electron systems are not very sensitive to these moderate deviations from planarity. The present calculation based on the planarity approximation seems to be sufficient for our purpose to select the appropriate structure of photooxygenation product. The calculated results indicate that the structure **3a** is the most probable one because the sum of two self-polarizabilities corresponding to this structure is larger than the pair self-polarizabilities corresponding to the other structures. Thus we may be able to disregard **3c**, **3d**, and **3e** from the possible structures of the endoperoxide.

It may be of some interest to note that although the sums of self-polarizabilities of para-positions corresponding to the structures **3a**, **3b**, and **3c** (0.999, 0.899, and 0.864, respectively) are similar to the corresponding values of anthracene (1.052 for 9,10-positions and 0.908 for 1,4-positions), the value of the self-polarizability of the 8-(and 16-) position of dibenzo[*a,j*]perylene, 0.604, is much larger than that for the 9-position of anthracene (0.526) and even larger than the value, 0.601, of the very reactive 6-(and 13-) position of pentacene. This may be the reason why dibenzo[*a,j*]perylene is so liable to react with singlet oxygen. The calculated values of free valence, which are given in Table 3, also suggest that 8-(and 16-) position is very reactive.

Thus we presume that the course of the reaction is as follows.



The second step from (A) to (B) should be very fast because of the enhanced density of reacting electron as a result of the first step reaction.

Further, we tried to see if the observed spectra of the photooxygenation product is compatible with this structure. Because of the high sensitivity of dibenzo[*a,j*]perylene to light and the instability of its photooxygenation product, it was difficult to obtain its correct spectra by a single run of the experiment. Figure 4 shows the spectrum composed of several experimental data.

The spectrum has some ambiguity in two regions. First, we could not completely bleach the region longer than 450 nm because the thermal decomposition of the oxygenation product brought about the reverse reaction and furthermore because the oxygenation product was also gradually decomposed, probably by further photochemical reaction,⁷⁾ to give some unknown final product which had a long absorption tail in this region. But it is certain that there is at most only

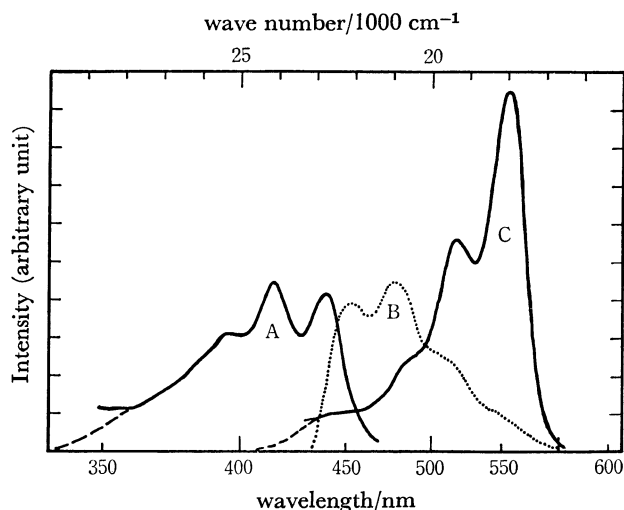


Fig. 4. Absorption and fluorescence spectra of photo-oxygenation product.

A: Corrected absorption spectra, benzene solution, B: fluorescence spectra, benzene solution, C: absorption spectra of dibenzo[*a,j*]perylene, the concentration of which is the same as A.

very weak absorption in this region, which can not be assigned to any allowed transitions. Another evidence to assure that the endoperoxide has no allowed absorption band in the region longer than 450 nm is that a fluorescence spectrum, which shows a good mirror image relation with the new absorption band between 380 and 450 nm, was observed for the partly

photobleached benzene solution of dibenzo[*a,j*]perylene (Fig. 4).

Since the absorption bands in the long wavelength region of the spectra of such endoperoxides are considered to be due to π - π^* transitions, we calculated the transition energies for the conjugated π -electron systems as drawn with thick lines in Fig. 3 on the basis of the P-P-P method. From the consideration of self-polarizabilities and free valences, it is sufficient to consider only the two structures, 8,12b-endoperoxide (**3a**) and 1,4-endoperoxide (**3b**).

The results of the calculation are shown in Table 2. The observed transition energies of benzo[*a*]perylene and 9-phenylanthracene, which have similar π -conjugation systems as those of **3a** and **3b**, respectively, are also shown in Table 2 together with the transition energies of related compounds, dibenzo[*a,j*]perylene and perylene. It is well-known that there are many factors that prevent a precise comparison between the observed and calculated results. But the overall correspondence is fairly good as is shown in Table 2.

Firstly, we assume that the structure of the photo-oxygenation product corresponds to **3b**. Both the calculated results and observed spectra of benzo[*a*]perylene predict that 1,4-endoperoxide (**3b**) should show the longest wavelength absorption band (so-called p-band) near 500 nm (20000 cm^{-1}). This value is rather larger than the observed one for the photo-oxygenation product, 435 nm. Furthermore, the observed oscillator strength for p-band of the photo-oxygenation product (about 80% of the p-band of

TABLE 2a. ELECTRONIC TRANSITIONS FOR STRUCTURES DEPICTED IN Fig. 3 AND RELATED COMPOUNDS
The energies in wave number (cm^{-1}), and oscillator strength (in parenthesis).

	Calcd ^{a)}				Obsd	
	9-Phenylanthracene type structure (Fig. 5a)				9-Phenylanthracene ^{d)}	Photooxygenation product ^{e)}
$\beta^{*b)}$	-2.38	-2.00	-1.50	-1.00	(small, ≈ 0)	
$\theta^c)$	0	32.8	50.9	65.1	($\approx 90^\circ$)	($\approx 60^\circ$, see text) ^{f)}
p-Band	20999 (1.02)	21485 (0.98)	22208 (0.91)	23032 (0.84)	25900 (0.15) ^{g)}	22750 (0.86) ^{h)}
α -Band	28278 (0.0)	28539 (0.0)	28883 (0.0)	29221 (0.0)		
	34430 (0.07)	34861 (0.06)	35454 (0.05)	36066 (0.03)		
	35009 (0.14)	35401 (0.14)	35950 (0.14)	36541 (0.13)		
	36629 (1.00)	37054 (1.05)	37631 (1.13)	38219 (1.22)		
β -Band	39766 (1.12)	40058 (1.12)	40436 (1.11)	40795 (1.08)		

a) Approximations for the calculations are as follows. i) The P-P-P method using the electron repulsion integral γ by Nishimoto and Mataga. $\beta = -2.38\text{ eV}$. ii) CI among 36 one electron excitation configurations. iii) Regular hexagonal structure with the C-C bond length of $1.397\text{ \AA}$. b) The resonance integral between the 9-carbon atom of the anthracene skeleton and the 1'-carbon of the phenyl group. c) The angle between the phenyl and anthracene skeleton planes, calculated from the approximate relation $\beta^* = \beta \cos \theta$. d) I. B. Berlman, "Handbook of fluorescence spectra of aromatic molecules," 2nd ed, Academic Press, New York (1971), p. 363. e) Present observation, see Fig. 4. f) Obtained by the graphic interpolation of the calculated θ -wave number relations. g) Calculated from the spectra reported in Berlman's book cited in d), based on the relation $f = 4.02 \times 10^{-9} \int \epsilon d\nu$. See the footnote**) in the text. h) Calculated from the spectra shown in Fig. 4 as is described in the footnote**) in the text. Almost the same value is obtained by the interpolation of the calculated θ -oscillator strength relation.

TABLE 2b. ELECTRONIC TRANSITIONS FOR STRUCTURES DEPICTED IN Fig. 3 AND RELATED COMPOUNDS

Benzo[<i>a</i>] perylene		Dibenzo[<i>a,j</i>]perylene		Perylene	
Calcd ^{a)}	Obsd	Calcd ^{a)}	Obsd ^{c)}	Calcd ^{a)}	Obsd ^{b)}
20830 (p-band) (0.96)	19880	18603 (p-band) (1.07)	18320	24553 (p-band) (1.00)	23000
29187 (α -band) (0.0)	29500	28705 (α -band) (0.0)	27000	30842 (α -band) (0.0)	
29697 (0.0)		34500 (0.20)		41920 (β -band) (1.80)	39600
30120 (0.02)		37333 (β -band) (2.03)	34480		
34560 (0.02)					
37193 (0.50)					
39153 (β -band) (1.34)	36230				
40160 (0.36)					

a) The approximations used for calculations are the same as in Table 2a. b) R. S. Becker, *J. Chem. Phys.*, **38**, 2144 (1963). c) This work and E. Clar, "Aromatic hydrocarbons, Academic Press, New York (1964), Vol. 2, p. 43.

dibenzo[*a,j*]perylene^{††} is considerably smaller than the calculated value for the p-band of benzo[*a*]perylene (about 90% of the p-band of dibenzo[*a,j*]perylene).

On the other hand, as we can see in Table 2, the calculated transition energy and oscillator strength of the 9-phenylanthracene type structure (corresponding to 8,12b-endoperoxide, **3a**), agree fairly well with the observed ones, if its phenyl plane has a proper angle (about 60°) with the plane of anthracene skeleton.

Of course, these agreements should not be taken too seriously since the adopted model of the molecular structure holds only the minimum characteristics of the endoperoxide and neglects all the finer details belonging to the real endoperoxide molecule and also because of the well-known limitations of MO calculations. Nevertheless all the observed data and calculated results seem to lead to the conclusion that the photooxygenation product of dibenzo[*a,j*]perylene is 8,12b-endoperoxide.^{†††}

As has been already mentioned, the molecular structure of dibenzo[*a,j*]perylene should be such as depicted in Fig. 5a.

O₂ may attach this hydrocarbon as illustrated in Fig. 5b; the angle between phenyl (A) plane and the anthracene plane should increase owing to the increased

^{††} This value was estimated from the ratio of area under each absorption band shown in Fig. 4, using the following formula

$$f = 4.02 \times 10^{-9} \int \epsilon d\nu$$

where *f* is the oscillator strength, ϵ the decadic molar extinction coefficient (l/mol cm), and $\bar{\nu}$ the wave number in cm⁻¹.

^{†††} It is reported that helianthrene is most probably attacked by the singlet oxygen at similar positions.²⁾

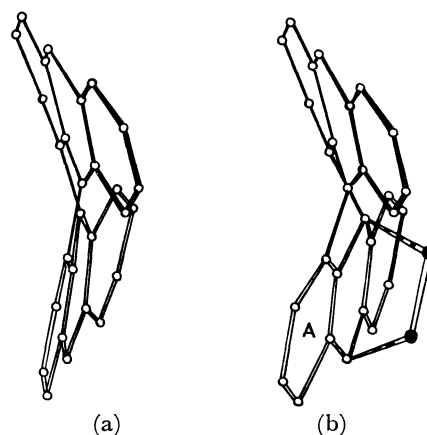
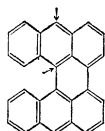
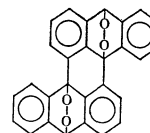


Fig. 5. Possible three dimensional structures of dibenzo[*a,j*]perylene and its photooxygenation product (8,12b-endoperoxide). a: Dibenzo[*a,j*]perylene, b: 8,12b-endoperoxide. ○: Carbon, ●: oxygen.

sp³ nature of the bonds extending from the 8- and 12b-carbon atoms and also owing to the steric hindrance of the H-atoms bonded to the 12- and 13-carbon atoms. Thus we can explain the rather high value of the angle, 60°, that has been predicted from the calculation. This structure also answers the question why a doubly photooxygenated product such as



was not obtained, which seems to be quite probable considering the well-known reactivity of 9-phenylanthracene to singlet molecular oxygen. The second molecular oxygen, if attached to the 8,12b-endoperoxide, will introduce intolerable steric hindrance,

TABLE 3. RATES OF THE OXYGEN DETACHMENT FROM 8,12b-ENDOPEROXIDE OF DIBENZO[*a,j*]PERYLENE

$\frac{T}{K}$	Rate $\frac{s^{-1}}$	
	in benzene	in ethanol
318	3.4×10^{-4}	
323	5.2×10^{-4}	
328	9.0×10^{-4}	
333	1.7×10^{-3}	7.2×10^{-4}
338	2.6×10^{-3}	1.2×10^{-3}
343	4.0×10^{-3}	1.9×10^{-3}
348		3.1×10^{-3}

and the double-photooxygenation product may be unstable and may decompose rapidly.^{†††}

The rate of O₂ detachment from the endoperoxide are shown in Table 3.

The detachment was monitored with the increasing band at 556 nm in benzene (and 546.5 nm in ethanol) of the recovered hydrocarbon and obeyed the first-order reaction scheme fairly well. The rate depends strongly on temperature and its temperature dependence seems to be explained by the existence of an activated transient state. The activation energy was calculated from the data in Table 3 to be 21.4 ± 0.5 kcal/mol in benzene and 22.5 ± 0.5 kcal/mol in ethanol. The frequency factor was also calculated to be $1.9 \times 10^{11} \text{ s}^{-1}$ in benzene and $4.9 \times 10^{11} \text{ s}^{-1}$ in ethanol, and these values suggest that the O₂-detachment reaction is spin allowed. The activation energy can be explained by the fact that the endoperoxide ground state necessarily correlates endothermically with an excited state of composite system A (Ground State) + O₂ (¹Δ_g) owing to spin conservation as is illustrated in Fig. 6. It is interesting that the observed activation energy is almost the same as the energy of the singlet O₂ ¹Δ_g state (22.5 kcal/mol), even if it might be only an accidental coincidence. Thus it may be possible that O₂ is released from the oxygenated hydrocarbon in its ¹Δ_g singlet state,¹⁴ but this must be clarified by further investigation.

Finally, we report a preliminary measurement of the overall efficiency of the present photooxygenation reaction. Though unfortunately, we could not afford to perform detailed measurements of lifetimes of A*(S), A*(T), and O₂(¹Δ_g) that are necessary to analyse each step of complicated photooxygenation reactions, we measured only the overall quantum efficiency of the photooxygenation upon irradiation of benzene solution by 556 nm under atmospheric pressure. The apparent overall quantum efficiency depended moderately on the concentration of dibenzo[*a,j*]perylene. They were *ca.* 1/30 for $7.2 \times 10^{-6} \text{ mol/dm}^3$ and *ca.* 1/45 for $5.6 \times 10^{-6} \text{ mol/dm}^3$. These values were about fifteen times larger than those for rubrene photooxygenation

^{†††} It has been reported that, similar hydrocarbons, dimethoxyhelianthrene and dibenzoyloxyhelianthrene uptake equimolar molecular oxygen rapidly, but further photooxygenation takes place only very slowly leading to final decomposition products.⁷⁾

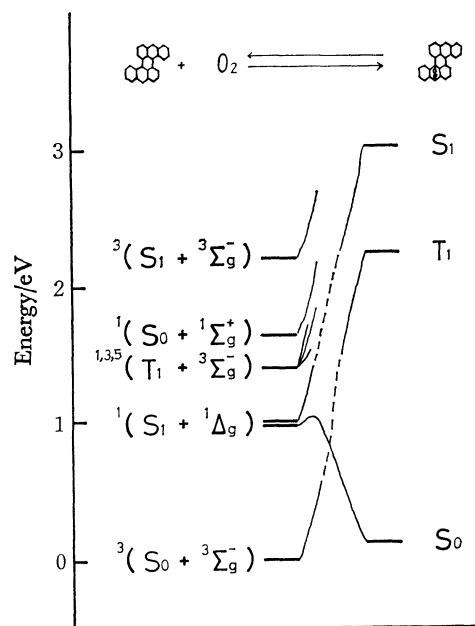


Fig. 6. State correlation diagram depicting the photooxygenation of dibenzo[*a,j*]perylene and thermal deoxygenation of the photooxygenation product, 8,12b-endoperoxide. The relative energies of the states were estimated from spectroscopic data and the activation energy for the reaction as is given in the text.

measured under similar conditions, and indicates that sensitized ¹Δ_gO₂ production may be quite efficient in this system. Assuming that the efficiency of ¹Δ_gO₂ production by the energy transfer from triplet dibenzo[*a,j*]perylene is nearly 100%,^{1,2)} and using the reported lifetime, 24 μs, of the O₂ ¹Δ_g state in benzene, we obtained $2 \times 10^8 \text{ dm}^3/\text{mol s}^{-1}$ as a lower limit of *k*, the rate of the reaction A(G) + O₂(S, ¹Δ_g) → AO₂.

Finally, it might be better to mention that the application of NMR, IR, and X-ray crystallography, which are very powerful methods for structural analysis in many fields of organic chemistry, is presently very difficult for unstable derivatives of large condensed aromatic hydrocarbons.

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shape as shown in Fig. 4 and the calculated oscillator strength as given in Table 2. The corresponding value by Clar is about 3.2×10^{-4} l/mol cm in benzene. The true value may be between these two values.

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