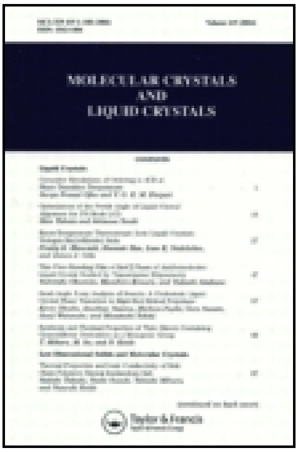

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X-Ray Crystallographic Analysis of the Endo-Peroxide of Anthra[1,9-b c:4,10-b′c′]Dichromene

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X-RAY CRYSTALLOGRAPHIC ANALYSIS OF THE ENDOPEROXIDE OF ANTHRA[1,9-*bc*:4,10-*b'c'*]DICHROMENE

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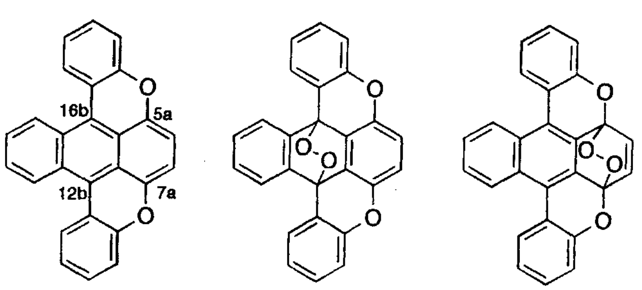
Abstract X-ray crystallographic analysis of the single crystals of endoperoxide of anthra[1,9-*bc*:4,10-*b'c'*]dichromene (**1**) has revealed the positions of singlet oxygen addition to **1**. The sites of oxygen attack were 9- and 10-positions of anthracene moieties but not 1- and 4-positions, coincided with the prediction from the coefficients of highest occupied molecular orbital calculated by AM1 or PM3 method.

INTRODUCTION

Addition of singlet oxygen to aromatic compounds has attracted much attention for their utilization to the photochromic systems. The regiospecificity accompanied with the addition of oxygen is altered by introduction of functional groups and it is sometimes difficult to determine the positions. The structures of the endoperoxides (colorless forms) of benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene and its analogues (colored forms) are easily determined by ^{1}H-^{1}H COSY NMR[1]. The structure of endoperoxide of anthra[1,9-*bc*:4,10-*b'c'*]dichromene (**1**) has been reported as **2**, however, the structure represented as **3** has not thoroughly been denied.[2] In this study, we report positions of singlet oxygen addition to **1** determined by the X-ray crystallographic method and discuss these results with the prediction by molecular orbital calculations.



1 **2** **3**

FIGURE 1 Anthra[1,9-*b,c*:4,10-*b'c'*]dichromene (**1**) and its possible endoperoxides (**2**, **3**)

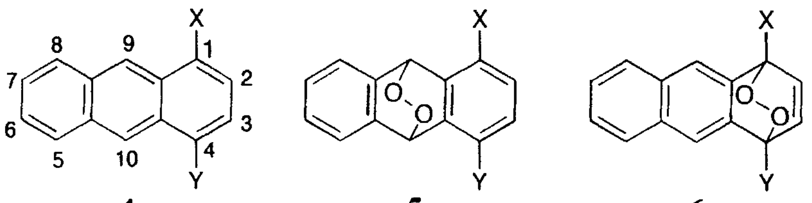
METHOD

Materials

Compound **1** was synthesized according to the procedure of Schmidt .[2] A toluene solution of **1** was irradiated using a 300 W tungsten lamp with cooling by ice bath. The solution turned from purple to light yellow. Recrystallization of the evaporated residue from toluene produced the endoperoxide as white precipitates.

Computational Studies

A starting geometry of **1** was obtained by molecular mechanics[3] using CAChe.[4] On the basis of the obtained geometry, the further optimization was performed by AM1[5] and PM3[6] method in MOPAC.[7] Similar full geometry optimization of the endoperoxide **2** and **3** were performed using initial coordinates obtained from the optimized geometry of **1**. The electronic states of endoperoxides of anthracene derivatives, **4a**-**4c**, were calculated by PPP-PC[8] because their geometries are planar.



4 **5** **6**

FIRURE 2 Anthracene and its derivatibes

a: X=H, Y=H
b: X=OCH_3, Y=H
c: X=OCH_3, Y=OCH_3

X-ray Crystallographic Analysis

The single crystals of the endoperoxide were obtained by slow evaporation of the carbontetrachloride solution in a dark place. A clear rod crystals with dimensions 0.5 x 0.4 x 0.2 mm was used as a sample for X-ray analysis. The epoxy coating was performed to prevent the crystal from any decomposition. Data collection and lattice parameters were measured at ambient temperature on a Mac Science MXC 3K four-circle diffractometer by using graphite monochromatized Cu Kα radiation. Three standard reflections showed gradual decrease through the data collection even after epoxy coating. 5418 reflections ($4 < 2\theta < 130$) were measured and 2993 independent reflections ($Fo > 3\sigma(Fo)$) were used for analysis. Absorption correction was not applied.

RESULTS AND DISCUSSION

Semi-empirical Molecular Orbital Method

Photooxygenation reaction of aromatic compounds are generally described as follows.10) *Ar* and *S* mean the condensed aromatic compound and the sensitizer, respectively.

Singlet oxygen $^1O_2$ is generated by energy transfer from Ar^* and/or S^* excited by photoirradiation. Addition of $^1O_2$ to a ground-state *Ar* produces the endoperoxide *ArPO.*

$$Ar \xrightarrow{h\nu} Ar^* \qquad (1)$$

$$S \xrightarrow{h\nu} S^* \qquad (2)$$

$$Ar^* / S^* + {}^3O_2 \longrightarrow Ar / S + {}^1O_2 \qquad (3)$$

$$O_2 + Ar \longrightarrow ArPO \qquad (4)$$

As the addition of a singlet oxygen to the aromatic substrate is a Diels-Alder type reaction,11) the addition is considered to occur at the maximum positions of the absolute HOMO coefficient.

First, we considered the planar anthracene derivatives for simplicity. Introduction of methoxy groups to 1- and 4-positions altered the electronic property of the anthracene units. In **4a** and **4b**, 9,10-positions have the largest populations of the absolute coefficients of the HOMO, whereas in **4c** the positions changes to the 1,4-positions (FIGURE 3). These calculations suggest that **4a** and **4b** produce the endoperoxide of type **5**, whereas **4c** produce the endoperoxide of type **6**. Indeed the photooxygenation of **4a** and **4b** provide the endoperoxide **5a** and **5b**, respectively, and **6c** was obtained from **4c**9) as predicted by MO calculations.

Calculation of the absolute values of HOMO coefficient of colored form **1** indicates the maximum populated positions of HOMO coefficient are at 12b- and 16b-positions (FIGURE 4). Therefore the positions of singlet oxygen addition should be predicted as 12b and 16b.

The heats of formation of **2** and **3** calculated by AM1 method were 95.2 and 101.5 kcal mol^{-1}, respectively. Thermodynamically, compound **2** seems more likely to be produced by photooxygenation than compound **3**.

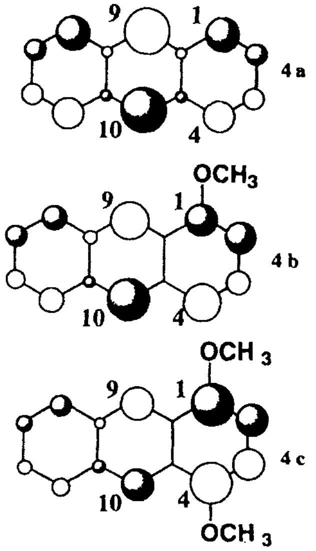


FIGURE 3 The coefficients of HOMO in **4a**-**4c**; Coefficients at 1- and 9-positions in **4a** correspond to -0.304 and +0.438, respectively.

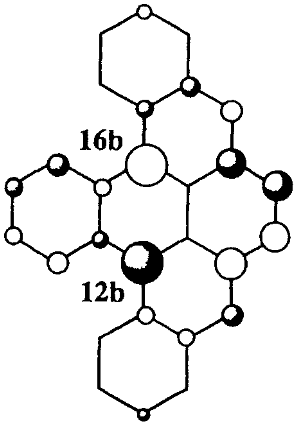


FIGURE 4
HOMO coefficients of **1**

X-ray Crystallographic Analysis

Crystal Data: $C_{26}H_{14}O_8 \cdot 2CCl_4$, $M = 698.04$, monoclinic, space group $P2_1/a$, $a = 15.610(3)$ Å, $b = 25.314(5)$ Å, $c = 7.382(2)$ Å, $\beta = 100.66(2)°$, $V = 2867(1)$ Å^3, $Z = 4$, $Dc = 1.62$ g cm^{-3}; final conversion $R = 13.2$ %.

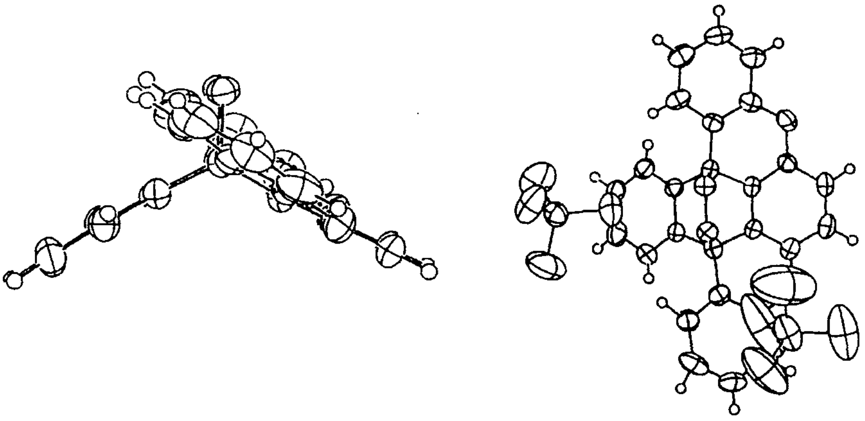


FIGURE 5 ORTEP drawing of endoperoxide **2**

The X-ray crystallographic analysis shows that additional positions of a singlet oxygen were the carbon atoms at 12b- and 16b-positions, which located at the center of anthracene ring (FIGURE 5). The molecules are folded about 120 degrees on the two sp^3 carbon atoms on which a molecule of singlet oxygen is attached. The steric hindrance between hydrogen atoms at 1- and 16- positions, and 12- and 13-positions in compound **1** is canceled by this folding. It was revealed that the carbontetrachloride molecules are included in the crystal (**2** and carbontetrachloride are in the ratio of 1:2). The carbontetrachloride molecules are located in the cavity made from folded **2**. There exist no short distances between host **2** and guest carbontetrachlorides. These molecules are held together only by van der Waals interactions.

The bond lengths and the bond angles of **2** defined by non-hydrogen atoms analysis were determined by X-ray crystallographic analysis and compared with those calculated by AM1 and PM3 methods. The mean differences of bond lengths between X-ray crystallographic analysis and AM1 method, and between the former analysis and PM3 method are 0.038Å and 0.026Å, respectively.

The O-O length (1.500(9) Å in **2**) determined by X-ray crystallographic analysis is closer to the value of 1.582 calculated by PM3 method than that of 1.303 calculated by AM1 method.

CONCLUSION

The positions of singlet oxygen addition to **1** revealed by X-ray crystallographic analysis coincided with the predicted positions by AM1 or PM3 molecular orbital calculation. The coincidences between observed and calculated sites of singlet oxygen attack were studied for the benzodixanthene derivatives[12, 13) and the diphenanthroperylene derivatives.[14) The result obtained here provides the validity of prediction of regiospecificity by molecular orbital calculations for the large distorted aromatics such as **1** to give endoperoxide.

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