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Crystal Structure and Thermodynamical Behavior of Tetrabenzo[*de,hi,op,st*]pentacene Endoperoxide

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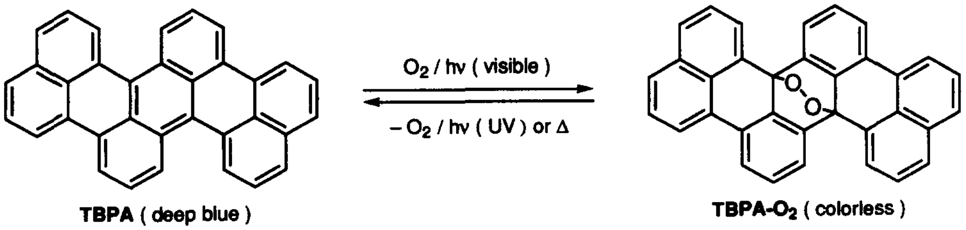
Abstract: The crystal structure of an endoperoxide of tetrabenzo[*de,hi,op,st*]pentacene (TBPA-O_2) was determined by X-ray crystallography. The unusually long O-O and C-O bonds were rationalized by the characteristic molecular structure of TBPA-O_2. The photochromic behavior between TBPA-O_2 and TBPA was discussed based on the enthalpy difference between TBPA-O_2 and TBPA + O_2 and the thermodynamic parameters of the extrusion reaction of oxygen from TBPA-O_2.

Recently, much attention has been paid to the photochromic behavior of fulugide compounds and spiropyranes, particularly with reference to the π-bond switching of functional π-conjugated molecules[1] and the applicability to photo-memory devices.[2] Besides the above types of compounds, some condensed polycyclic aromatics were also found to exhibit photochromic behavior. Reversible photo-oxidation of tetrabenzo[*de,hi,op,st*]pentacene (TBPA) is one of such examples.[3] The deep-blue color of TBPA fades on irradiating visible light, and the color recovers through UV irradiation. This photochromic behavior is rationalized in terms of a reversible interconversion between TBPA and its endoperoxide (TBPA-O_2) (Scheme 1). By absorbing visible light, TBPA-O_2 is formed by the reaction of TBPA with $^1O_2$, which is presumably formed through an autosensitization of TBPA. On the other hand, UV irradiation of TBPA-O_2 regenerates TBPA through an extrusion of O_2. The latter process also occurs by thermal decomposition. Although examination of the structure and reactivity of endoperoxides is crucial to understanding their photochromic



Scheme 1. Reversible interconversion between TBPA and TBPA-O_2

behavior, the crystal structure of endoperoxides of condensed polycyclic aromatics has scarcely been elucidated.[4] Here we report the crystal structure of TBPA-O_2 and the thermodynamic parameters of the reversible interconversion between TBPA-O_2 and TBPA + O_2, and interpret the efficient photochromic behavior based on the characteristic molecular structures of both TBPA-O_2 and TBPA.

Single crystals of TBPA-O_2 were obtained by recrystallization from benzene. X-Ray diffraction data of the single crystal in a sealed tube were collected at room temperature on a Rigaku AFC-5S four-circle diffractometer. The structure of TBPA-O_2 was solved by direct methods (MITHRIL) and refined by a full-matrix least-squares refinement (SHELX93).[5] The crystal structure of TBPA-O_2 is shown in Fig. 1. In the cavity formed by the bulky TBPA-O_2, two benzene molecules are incorporated per one endoperoxide molecule. Figure 2 shows the molecular structure of TBPA-O_2 : Oxygen atoms bridge over 9b and 18b carbon atoms, and the bridging positions are in accord with the proposed structure based on the spectroscopic data.[6] Since hybridization of carbons at 9b and 18b changes by addition of singlet oxygen, the endoperoxide has a bent molecular structure like triptycene. Pyramidilization of carbons at 9b and 18b, however, is considered to be incomplete because of the fused ring structure. The p-character of the C–O bond is evaluated to be ca 86% based on the bond angle of the bridgehead carbon (the average of ∠O-C-C is 105°). Therefore, the C-O bond lengths are elongated to be 1.492(8), 1.516(8) Å. The O-O bond length (1.496(5) Å) of the endoperoxide moiety is also found to be unusually long. The elongated O-O bond may be caused by reducing the electronic repulsion between lone pairs of electrons on the oxygen atoms in an eclipsed configuration, the dihedral angle of C-O-O-C being 1.3°. Incidentally, the elongated bond lengths of the O-O and C-O bonds are commonly observed in cyclic peroxides.[7]

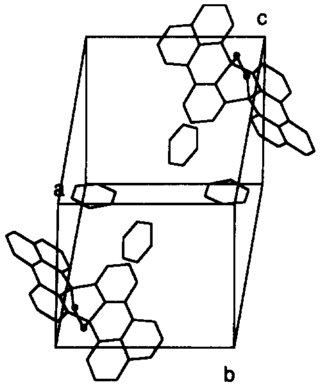


Fig. 1. Crystal structure of TBPA-O_2·$(C_6H_6)_2$ Hydrogen atoms are omitted for clarity.

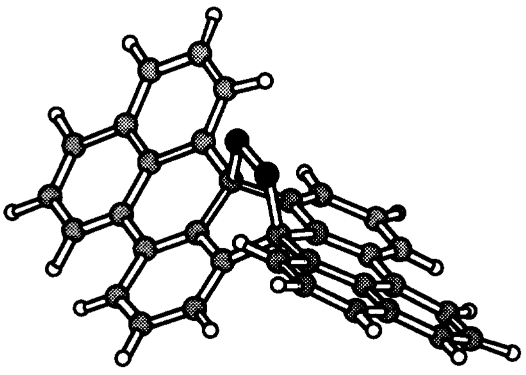


Fig. 2. Molecular structure of TBPA-O_2

Thermodynamic parameters of TBPA-O_2 were determined by calorimetric and kinetic measurements and were discussed comparing with those of the related species. The difference in enthalpy (ΔH_0) between TBPA-O_2 and TBPA + O_2 was evaluated to be +38 kJ/mol (endothermic) by differential scanning calorimetric measurements (Fig. 3). This value is larger than the corresponding enthalpy difference of +21 kJ/mol between 9,10-diphenylanthracene endoperoxide and 9,10-diphenylanthracene (DPA) and O_2.[8] The large difference in enthalpies between TBPA-O_2 and TBPA may be derived from the fact that the generated TBPA has a steric strain due to the overcrowded structure carrying bay regions.[6]

On the other hand, the activation energy of the extrusion of oxygen molecule from TBPA-O_2 was determined to be 147.4 kJ/mol by an Arrhenius plot of the first-order rate constants in *o*-xylene in the temperature range of 353 ~ 405 K,[9] and the activation enthalpy ($\overrightarrow{\Delta H^{\neq}}$) and the activation entropy of this process were evaluated to be 144 kJ/mol and +59.4 J/mol·K, respectively. Thus, the kinetic stability of TBPA-O_2 is considered to be reasonably high in spite of the presence of the elongated bonds in the endoperoxide moiety. A large positive value of the activation entropy suggests that TBPA-O_2 tends to produce $^3O_2$ rather than $^1O_2$.[8, 10] Taking account of the microscopic reversibility between generation of oxygen from TBPA-O_2 and addition of oxygen to TBPA,[8] and of the energy difference between $^3O_2$ and $^1O_2$ (~94 kJ/mol),[11] the activation enthalpy of addition of $^1O_2$ to TBPA ($\overleftarrow{\Delta H^{\neq}}$) was estimated to be 12 kJ/mol

This value is considerably smaller than the corresponding value of 21 kJ/mol for the addition of $^1O_2$ to DPA.[12] The smaller activation enthalpy may be derived from the distortion of the central benzene ring of TBPA into a boat form (Fig. 4b). This distortion (the bent angle of ca 15° degree) causes TBPA to proceed along the reaction coordinate to the direction for the addition of $^1O_2$.

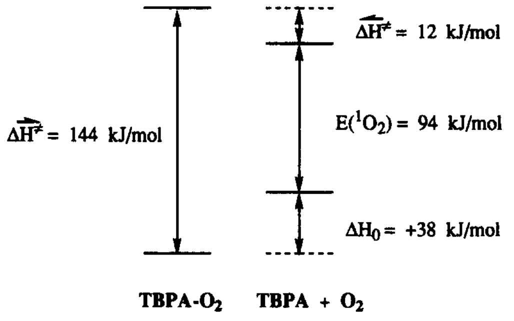


Fig. 3 Thermodynamic parameters of the reversible interconversion between TBPA-O_2 and TBPA

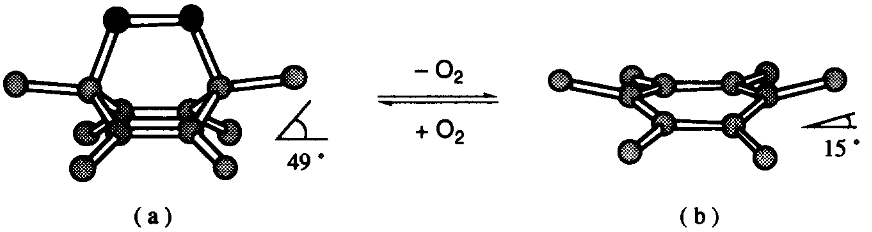


Fig. 4 Partial molecular structure of TBPA-O_2 and TBPA based on their crystallographic data. Bent angle of the central ring of each compound is shown in the figure.
(a) Endoperoxide moiety in TBPA-O_2 (Black balls represent oxygen atoms).
(b) Deformed central ring of TBPA.[6]

In conclusion, we have determined the crystal structure of TBPA-O_2 and the thermodynamic parameters of the relevant chemical processes. The efficient fading of colors of TBPA is presumably due to the small activation enthalpy for the addition of singlet oxygen generated by an autosensetization effect of TBPA. Moreover, the formed TBPA-O_2 has a reasonably high kinetic stability. Thus, the photochromic system of TBPA and TBPA-O_2 may be applicable to switching the functionalities of the π-conjugated molecules.

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5. *Crystal data* : $C_{34}H_{18}O_2 \cdot (C_6H_6)_2$, *F.W.* = 614.74, triclinic, space group $P\bar{1}$,
   $a = 10.922(2)$, $b = 14.884(2)$, $c = 10.071(2)$ Å, $\alpha = 102.19(1)$, $\beta = 94.13(2)$, $\gamma = 88.87(1)°$, $V = 1596.1(4)$ Å^3, $Z = 2$, $D_c = 1.279$ g cm^{-3}. Cu-$K\alpha$ radiation (graphite monochromator, $\lambda = 1.54184$ Å). Final conventional R factors : $R[F^2 > 2\sigma(F^2)] = 0.0994$, $wR(F^2) = 0.2973$ for 2737 observed reflections and 495 parameters; $w = 1/[\sigma^2(F_O^2) + (0.3642P)^2 + 0.03P]$, where $P = (\max(F_O^2, 0) + 2F_C^2)/3$.
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10. Judging from a trapping experiment with tetraphenylcycropentadienone at 90°C for 72h as described in ref 7, the yield of $^1O_2$ from TBPA-O_2 was considered to be very low, because no cis-dibenzoylstilbene was obtained (The initial concentrations of TBPA-O_2 and tetraphenylcyclopentadienone in *o*-xylene were 8×10^{-4} and 8×10^{-3} mol/l, respectively).
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