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Molecular Geometry of the Photooxygenation Product of Diphenanthro[5,4,3-abcd:5′,4′,3′-jklm]perylene

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The photooxygenation of diphenanthro[5,4,3-abcd:5′,4′,3′-jklm]perylene (DPP) is investigated by using semi-empirical molecular orbital methods. It was shown theoretically that molecular oxygen (O_2) attaches to the central part of DPP, causing a large bend of the molecular plane. The experimental observation was reasonably explained on the basis of the calculated oscillator strengths of optically allowed transitions in DPP and photooxygenated DPP.

Diphenanthro[5,4,3-abcd:5′,4′,3′-jklm]perylene(DPP) is an undecacyclic condensed aromatic hydrocarbon which has an approximate two-fold symmetry axis along the direction perpendicular to the molecular plane (Fig. 1). DPP is photobleached in a solution by visible light irradiation. In fact, the intensity of the absorption transition to the first π-π^* state of DPP was strongly reduced on irradiation and a new absorption band appeared in the region of about 320–380 nm (Fig. 2).[1] This phenomenon can be interpreted as a photooxygenation reaction;[2] DPP reacts with singlet molecular oxygen O_2 ($^1\Delta_g$) to form an O_2 adduct (ODPP). ODPP releases the attached oxygen gradually at room temperature, reproducing DPP.

The molecular and crystal structures of DPP have been reported by Oonishi et al.,[3] whereas those of ODPP have not been reported. In order to investigate the molecular geometry of ODPP and the spectral changes due to the photooxygenation, we performed semi-empirical molecular orbital calculations.

All geometrical parameters were optimized without any symmetrical restrictions. The modified neglect of diatomic overlap (MNDO) method was adopted for geometry optimization with PM3 parameters. The complete neglect of differential overlap (CNDO/S) and configuration interaction (CI) method was adopted to the calculation of the oscillator strength. The MNDO-PM3 calculation

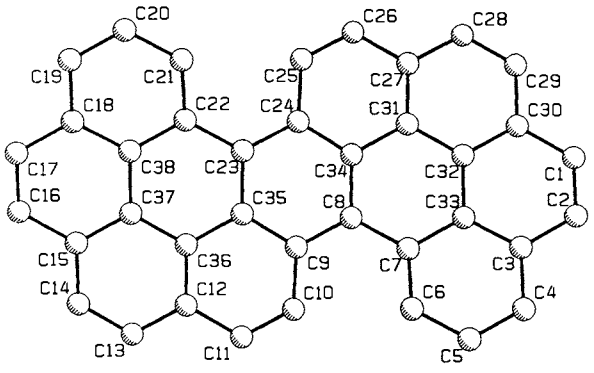

Fig.1. Molecular skeleton without hydrogen atoms and numbering scheme of DPP.

was performed with the MOPAC program.[4] For the CNDO/S-CI calculation, QCPE #174[5] was adopted; the electron repulsion part was modified as suggested by Banno and Nishimoto,[6] *i.e.*, $(rr|ss)=e^2/(XR_{rs} + C)$, where $(rr|ss)$ is the two electron–interaction integral over atomic orbitals ϕ_r and ϕ_s, e is the electronic charge, R_{rs} is the distance between two atoms to which the atomic orbitals belong, C is $2e/((rr|rr)+(ss|ss))$, and X is an adjustable parameter. In the case of DPP, X was 3.00; this value was taken so as to reproduce the feature of the absorption spectrum.

The geometrical parameters obtained theoretically are listed in Table 1. The parameters of ODPP were almost the same as those of DPP, except for some parameters leading to a bend of the molecular plane. The most stable molecular geometry of ODPP is shown in Figs. 3-5. An O_2 molecule attaches to the pair carbon atoms which have the largest π electron density of the highest occupied molecular orbital (HOMO), and it divides the large π systems of DPP into two equivalent small π systems. This is consistent with the speculation of Izuoka et al.[7] on the geometry of photooxygenated tetrabenzo-[*de,hi,op,st*]pentacene. It should be noticed that the O_2-attached carbon atoms form the sp^3 hybrid orbitals, causing a large bend of the molecular plane.

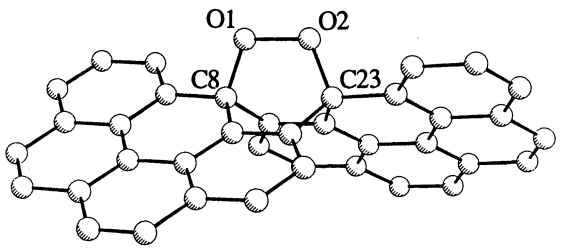

Fig.4. Perspective drawing of ODPP along the direction perpendicular to the plane going through C(8)–O(1)–O(2)–C(23). The bonds around C(8) and C(23) have the perfect sp^3 character.

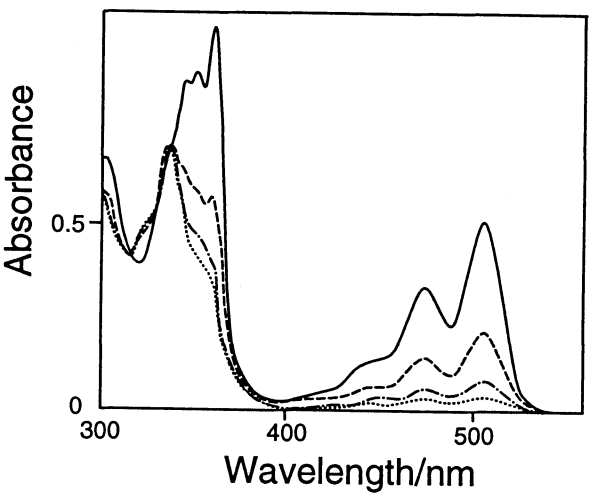

Fig.2. Change of absorption spectra in *o*-dichlorobenzene by visible light irradiation.
——— : Before irradiation,
– – – – : after 2 minutes irradiation,
– · – · – : after 5 minutes irradiation,
· · · · · · : after 30 minutes irradiation.

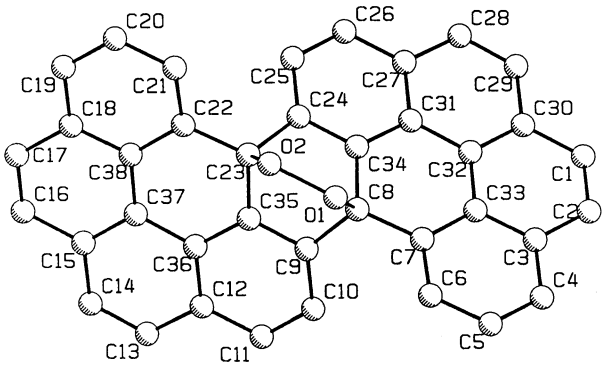

Fig.3. Molecular skeleton without hydrogen atoms and numbering scheme of ODPP.

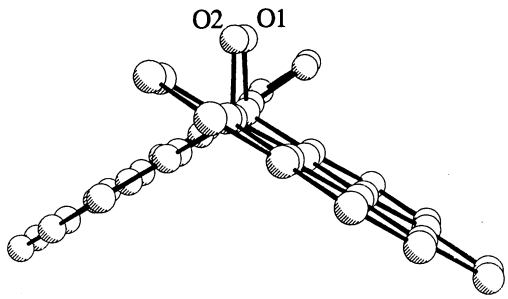

Fig.5. Perspective drawing of ODPP approximately along the O–O bond.

Table 1. Optimized Geometries of DPP and ODPP

Bond distances /Å[a]	DPP	ODPP	Bond angles /° [b]	DPP	ODPP		DPP	ODPP
C(1)—C(2)	1.36	1.36	C(30)–C(1)—C(2)	120.6	120.4	C(22)–C(23)–C(35)	118.6	113.7
C(1)—C(30)	1.43	1.43	C(1)—C(2)—C(3)	120.9	121.1	C(24)–C(23)–C(35)	117.3	104.9
C(2)—C(3)	1.44	1.43	C(2)—C(3)—C(4)	120.7	120.6	C(23)–C(24)–C(25)	122.3	128.6
C(3)—C(4)	1.41	1.41	C(2)—C(3)—C(33)	119.6	119.8	C(23)–C(24)–C(34)	119.6	114.0
C(3)—C(33)	1.41	1.41	C(4)—C(3)—C(33)	119.7	119.7	C(25)–C(24)–C(34)	118.1	120.0
C(4)—C(5)	1.38	1.37	C(3)—C(4)—C(5)	119.6	120.2	C(24)–C(25)–C(26)	122.4	119.5
C(5)—C(6)	1.40	1.41	C(4)—C(5)—C(6)	120.6	120.5	C(25)–C(26)–C(27)	120.5	121.1
C(6)—C(7)	1.39	1.38	C(5)—C(6)—C(7)	121.6	120.7	C(26)–C(27)–C(28)	120.7	122.5
C(7)—C(8)	1.46	1.51	C(6)—C(7)—C(8)	123.0	120.0	C(26)–C(27)–C(31)	119.0	119.2
C(7)—C(33)	1.42	1.42	C(6)—C(7)—C(33)	117.7	119.6	C(28)–C(27)–C(31)	120.3	118.3
C(8)—C(9)	1.41	1.53	C(8)—C(7)—C(33)	119.3	120.4	C(27)–C(28)–C(29)	120.6	120.7
C(8)—C(34)	1.41	1.52	C(7)—C(8)—C(9)	124.1	115.8	C(28)–C(29)–C(30)	120.3	121.3
C(9)—C(10)	1.44	1.40	C(7)—C(8)—C(34)	118.6	113.7	C(29)–C(30)–C(1)	120.8	121.1
C(9)—C(35)	1.42	1.39	C(9)—C(8)—C(34)	117.3	104.9	C(29)–C(30)–C(32)	119.7	119.6
C(10)–C(11)	1.35	1.38	C(8)—C(9)—C(10)	122.3	128.6	C(1)—C(30)–C(32)	119.5	119.3
C(11)–C(12)	1.43	1.41	C(8)—C(9)—C(35)	119.6	111.4	C(27)–C(31)–C(32)	119.0	121.1
C(12)–C(13)	1.42	1.43	C(10)–C(9)—C(35)	118.1	120.0	C(27)–C(31)–C(34)	120.8	118.9
C(12)–C(36)	1.40	1.41	C(9)—C(10)–C(11)	122.4	119.5	C(32)–C(31)–C(34)	120.2	120.0
C(13)–C(14)	1.37	1.36	C(10)–C(11)–C(12)	120.5	121.1	C(30)–C(32)–C(31)	120.2	119.1
C(14)–C(15)	1.42	1.43	C(11)–C(12)–C(13)	120.8	122.5	C(30)–C(32)–C(33)	120.2	121.1
C(15)–C(16)	1.43	1.43	C(11)–C(12)–C(36)	119.0	119.2	C(31)–C(32)–C(33)	119.5	119.9
C(15)–C(37)	1.40	1.39	C(13)–C(12)–C(36)	120.3	118.3	C(3)—C(33)–C(7)	120.5	119.4
C(16)–C(17)	1.36	1.36	C(12)–C(13)–C(14)	120.6	120.7	C(3)—C(33)–C(32)	119.0	118.3
C(17)–C(18)	1.44	1.43	C(13)–C(14)–C(15)	120.3	121.3	C(7)—C(33)–C(32)	120.5	122.3
C(18)–C(19)	1.41	1.41	C(14)–C(15)–C(16)	120.8	121.1	C(8)—C(34)–C(24)	120.9	115.0
C(18)–C(38)	1.41	1.41	C(14)–C(15)–C(37)	119.7	119.6	C(8)—C(34)–C(31)	120.0	123.7
C(19)–C(20)	1.38	1.37	C(16)–C(15)–C(37)	119.5	119.3	C(24)–C(34)–C(31)	119.1	121.3
C(20)–C(21)	1.40	1.41	C(15)–C(16)–C(17)	120.6	120.4	C(9)—C(35)–C(23)	120.9	115.0
C(21)–C(22)	1.39	1.38	C(16)–C(17)–C(18)	120.9	121.1	C(9)—C(35)–C(36)	119.1	121.3
C(22)–C(23)	1.46	1.51	C(17)–C(18)–C(19)	120.7	120.6	C(23)–C(35)–C(36)	120.0	123.7
C(22)–C(38)	1.42	1.42	C(17)–C(18)–C(38)	119.6	119.8	C(12)–C(36)–C(35)	120.8	118.9
C(23)–C(24)	1.41	1.53	C(19)–C(18)–C(38)	119.7	119.7	C(12)–C(36)–C(37)	119.0	121.2
C(23)–C(35)	1.41	1.52	C(18)–C(19)–C(20)	119.6	120.2	C(35)–C(36)–C(37)	120.2	120.0
C(24)–C(25)	1.44	1.40	C(19)–C(20)–C(21)	120.6	120.5	C(15)–C(37)–C(36)	120.2	119.1
C(24)–C(34)	1.42	1.39	C(20)–C(21)–C(22)	121.6	120.7	C(15)–C(37)–C(38)	120.2	121.1
C(25)–C(26)	1.35	1.38	C(21)–C(22)–C(23)	123.0	120.0	C(36)–C(37)–C(38)	119.5	119.9
C(26)–C(27)	1.43	1.41	C(21)–C(22)–C(38)	117.7	119.6	C(18)–C(38)–C(22)	120.5	119.4
C(27)–C(28)	1.42	1.43	C(23)–C(22)–C(38)	119.3	120.4	C(18)–C(38)–C(37)	119.0	118.3
C(27)–C(31)	1.40	1.41	C(22)–C(23)–C(24)	124.1	115.8	C(22)–C(38)–C(37)	120.5	122.3
C(28)–C(29)	1.37	1.36	O(1)—C(8)—C(7)		107.5	O(2)—C(23)–C(24)		107.5
C(29)–C(30)	1.42	1.43	O(1)—C(8)—C(9)		107.5	O(2)—C(23)–C(35)		107.1
C(30)–C(32)	1.40	1.39	O(1)—C(8)—C(34)		107.1	O(2)—O(1)—C(8)		110.5
C(31)–C(32)	1.42	1.43	O(2)—C(23)–C(22)		107.5	O(1)—O(2)—C(23)		110.5
C(31)–C(34)	1.44	1.40						
C(32)–C(33)	1.43	1.44						
C(35)–C(36)	1.44	1.40						
C(36)–C(37)	1.42	1.43						
C(37)–C(38)	1.43	1.44						
O(1)—O(2)		1.58						
O(1)—C(8)		1.44						
O(2)—C(23)		1.44						

a) All C–H bond distances are 1.1Å . b) The bond angles related to hydrogen atoms are omitted.

The energies and oscillator strengths calculated for excitation from the ground state of DPP and ODPP are listed in Table 2; the energies are expressed in wavelength (nm) of light absorbed in the excitation. The longest absorption-wavelength of DPP is 516 nm and is much longer than that of ODPP, 389 nm. Both of DPP and ODPP absorb at the wavelength region 310–390 nm, though ODPP has much weaker absorption than DPP. Therefore, the followings are predicted theoretically: (1) the photooxygenation reaction reduces the absorption intensity of DPP, and (2) as the photooxygenation reaction proceeds, the absorption of ODPP can be observed gradually at shorter absorption wavelengths of DPP. These predictions agree well with the experimental results shown in Fig. 2.

Table 2. Excitation energies and oscillator strengths (f)

DPP		ODPP	
λ/nm	f	λ/nm	f
516.4	1.20	388.9	0.07
476.0	0.02	384.2	0.00
419.0	0.00	367.8	0.04
395.2	0.00	351.0	0.10
378.5	1.30	336.4	0.53
370.8	0.04	326.6	0.00
369.8	0.11	324.9	0.20
345.0	0.01	321.9	0.06
340.0	0.03	315.2	0.00
334.4	0.03	314.6	0.07
333.2	0.02		
328.6	0.00		
325.2	0.43		
316.8	0.01		
313.5	0.65		

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