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OXIDATION PRODUCTS OF 2-ARYLPHENANTHRO-[9,10-d]IMIDAZOLES – II

STRUCTURE AND PHOTOCHROMISM OF OXIDATION PRODUCTS OF 2-(4-METHOXYPHENYL)-PHENANTHRO-[9,10-*d*]IMIDAZOLE

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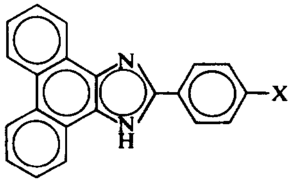
Abstract – By ferricyanide oxidation of 2-(4-methoxyphenyl)phenanthro[9,10-*d*]imidazole, three new photochromic compounds were obtained. These were 4-ethoxy-4H-, 4-methoxy-4H- and 2-methoxy-2H-phenanthro[9,10-*d*]imidazoles. These compounds gave the 2-(4-methoxyphenyl)-phenanthro[9,10-*d*]imidazolyl radical and acetaldehyde or formaldehyde by light irradiation. The imidazolyl radical dimerized gradually in the dark and the dimer dissociated to the imidazolyl radical on heating.

INTRODUCTION

In the course of our studies on the oxidation products of 2-arylphenanthro[9,10-*d*]imidazoles (1) it has been found[1,2] that various derivatives of 1 afford the corresponding dimers (2, X = H, Me and Cl) by ferricyanide oxidation, and three dimers exhibit characteristic thermochromism. Thus, a solution of the colorless dimer 2 exhibits a remarkable blue color on warming and the color disappears on cooling the solution.



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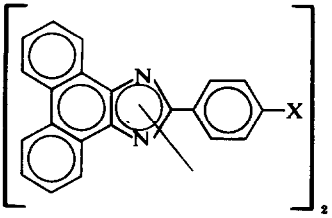

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The ferricyanide oxidation of 2-(4-methoxyphenyl)phenanthro[9,10-*d*]imidazole (1, X = OMe) did not afford the corresponding dimer, but yielded products of a new type. Some oxidation products did not show the thermochromism but showed the photochromic property.

The photochromic properties of bis(2,4,5-triphenylimidazolyl) (4) and its derivatives were extensively studied by Hayashi and Maeda.[3] They have clarified that the photochromic compound 4 is obtained from 2,4,5-triphenylimidazole (3), lophine, by ferricyanide oxidation and the photochromic property is due to a reversible dissociation of the dimer 4* into a radical 5 by light irradiation.

We studied the photochromic compounds derived from anisylphenanthro-imidazole 1 (X = OMe) and the mechanism of the photochromism, and found that the oxidation products have a structure quite different from that of the oxidation product of lophine (3).

RESULTS AND DISCUSSION

When an aqueous solution of potassium ferricyanide was added to a solution of anisylphen-

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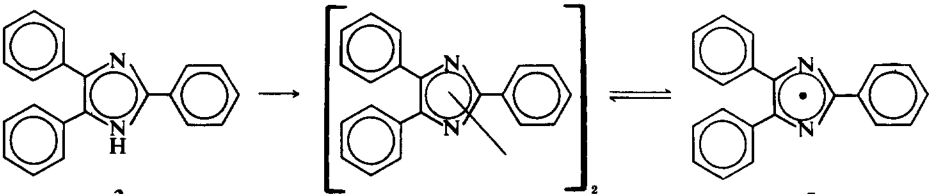
*The structure of 4 has been recently determined by Goto *et al.*[4]



3 4 5

anthro-imidazole 1 (X = OMe) in ethanolic potassium hydroxide, a deep blue color first appeared and then a light green precipitate separated gradually. The precipitate was washed with water and dried to a light-green solid. In the solid state, this substance showed an ESR signal which was enhanced by light irradiation, but no color change was noted by trituration.

When a light-green benzene solution of the solid was heated in a dim light, the green color and ESR signal was enhanced with a rise of temperature. On cooling in the dark, the color reverted to the original pale green accompanied by the decrease of ESR signal intensity. These facts seemed to suggest that the crude product had dual photochromic and thermochromic properties. Analysis revealed that the product consisted of more than two components, and two compounds, A and B, which were obtained in a pure state. Compound A exhibited photochromic but no thermochromic property both in solution and the solid state, but compound B exhibited neither thermochromism nor photochromism. A thermochromic compound which was expected to be present in the oxidation product could not be obtained in a pure state.

Structure of compound A. The UV spectrum of compound A showed absorption maxima at 261 (log ϵ: 4·58) and 317 (4·19) nm. This spectrum excluded the presence of the imidazolyl group in compound A, because 2-aryl- and 1,2-diarylphenanthro[9,10-*d*]imidazoles have the absorption maximum at the region 355–360 nm.[5]

The elemental analysis and the mass spectrum assigned the molecular formula, $C_{24}H_{20}N_2O_2$, to compound A. This composition indicates that an OEt group is incorporated into the starting anisylphenanthro-imidazole by oxidation. The presence of an OEt group was detected by the NMR spectrum.

The 100-MHz NMR spectrum of compound A in $CDCl_3$ (Fig 1) showed, in addition to aromatic protons at 7·25–8·50 and OMe protons at 3·88, a triplet (3H, $J = 7$ Hz) at 1·00 and a multiplet (2H) centered at 3·35 ppm. Irradiation of the Me group at 1·00 caused the multiplet centered at 3·35 to appear as an AB quartet ($J = 7{\cdot}1$ Hz). This revealed the presence of an OEt group in which the methylene group appeared as an AB of the ABX_3 system. This nonequivalence of methylene protons of OEt was observed when it was bonded at an assymetric C atom as in the case of ethyl isobutyl ether[6] and others.[7] Aromatic protons of the anisyl group appeared as a pair of doublets of $A_2'B_2'$ type ($J = 9$ Hz) at 7·05 and 8·45, and this assignment was confirmed by the double resonance. The remaining peaks between 7·25 and 8·00 ppm were assigned as phenanthreno protons. These assignments were confirmed by the deuterated compound 7, which was prepared for analysis

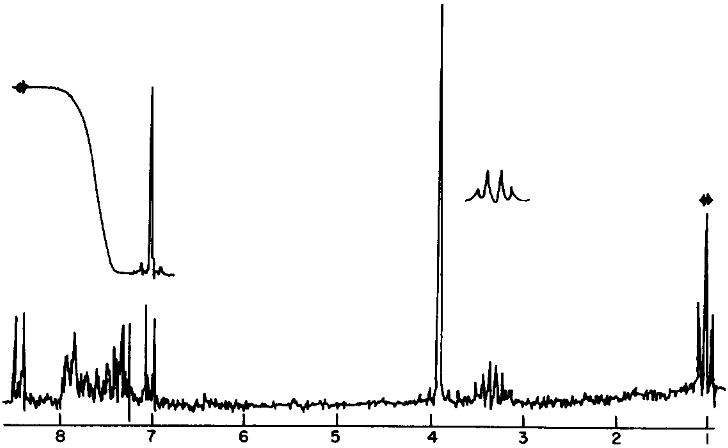
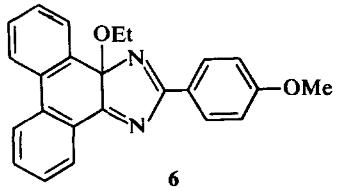


Fig 1. NMR spectrum of compound A in $CDCl_3$.

of the ESR spectrum.[8] The deuterated compound 7 showed only OEt (1·00, 3 35 ppm) and anisyl protons (3·88, 7·05 and 8·45 ppm) with the same coupling constants as compound A. The extremely down field resonance of two protons of anisyl group indicated that this group is attached to an sp^2 carbon bearing electronegative atoms. From these NMR features and the other spectral properties, structure 6 was deduced for compound A. The structure was further confirmed by ^{13}C-NMR spectrum (Fig 2 and Table 1).



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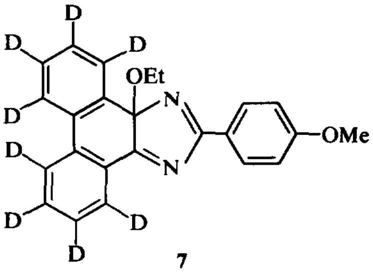

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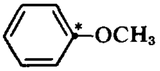
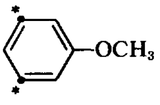
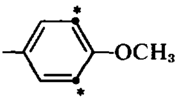
Table 1. The assignment of ^{13}C-NMR spectrum of compound A

No.	Height	Freq. (Hz)	ppm	Assignment (*)
1	30	1806·64	71·83	
2	23	2534 48	100·77	—
3	50	2551·86	101·44	Ph$^{\Delta}$
4	98	2586·36	102·83	
5	40	2632·14	104·65	Ph$^{\Delta}$
6	39	2650·45	105·38	
7	49	2667·23	106·05	
8	37	2671·81	106·23	
9	20	2684·02	106·72	—
10	51	2743·53	109·08	Ph$^{\Delta}$
11	48	2748·10	109·26	
12	54	2778·62	110·48	
13	20	2789·30	110·90	—
14	76	3036·49	120·73	
15	103	3936·76	156·53	CDCl$_3$
16	89	3968·81	157 80	
17	83	4000·85	159·07	
18	45	4373·16	173·88	—OC*H$_2$CH$_3$
19	40	4510·49	179·34	—OC*H$_3$
20	33	5516·05	219·32	—OCH$_2$C*H$_3$

Δ: Ph: carbon accompanying hydrogen at phenanthreno nucleus.

Structure of compound B. Compound B, $C_{24}H_{20}N_2O_3$, obtained from anisylphenanthroimidazole 1 (X = OMe) as a minor oxidation product, has one more O atom than compound A. The UV spectrum, λ_{max} 272 and 287 nm, showed the absence of a phenanthryl chromophore B. The NMR spectrum (Fig 3) of compound B in CDCl$_3$ indicated an OMe group at 3·80 (s, 3H) and an OEt group at 1·2 (3H, t, $J = 7$) and 4·33 (2H, q, $J = 7$). Two methylene protons of the OEt group are equivalent in contrast with the case of compound A. The aromatic protons of the *p*-anisyl group were observed at 7·56 (2H, d, $J = 9$ Hz) and 6·75 (2H, d, $J = 9$ Hz) as a pair of doublets of $A_2'B_2'$ type which were shifted up-field compared to those of compound A. The ortho protons of the aryl group of 2-arylphenanthro[9,10-*d*]imidazoles and 2-aryl-4H-imidazoles usually appear around 8·4 ppm.[2,4] These indicated the anisyl group of compound B was bonded to a saturated C atom in the phenanthro-imidazolyl skeleton. A multiplet centered at 8·45 ppm was assigned as the C_{11}-proton deshielded by the neighbouring oxygen. In the NMR spectrum of the deuterated compound 9 the multiplet at 8·45 ppm and multiplets between 6·8 and 7·7 ppm except the anisyl protons had disappeared. These spectral properties suggested structure 8 for compound B.

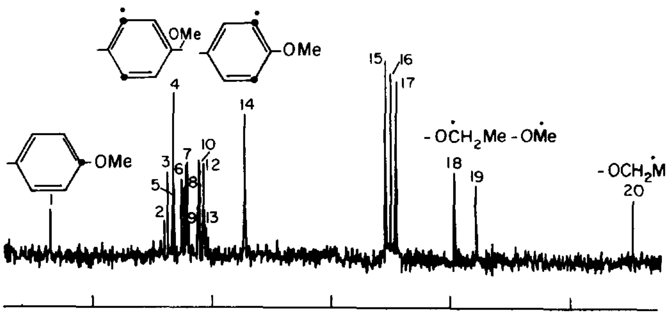


Fig 2. ^{13}C-FT-NMR spectrum of compound A.

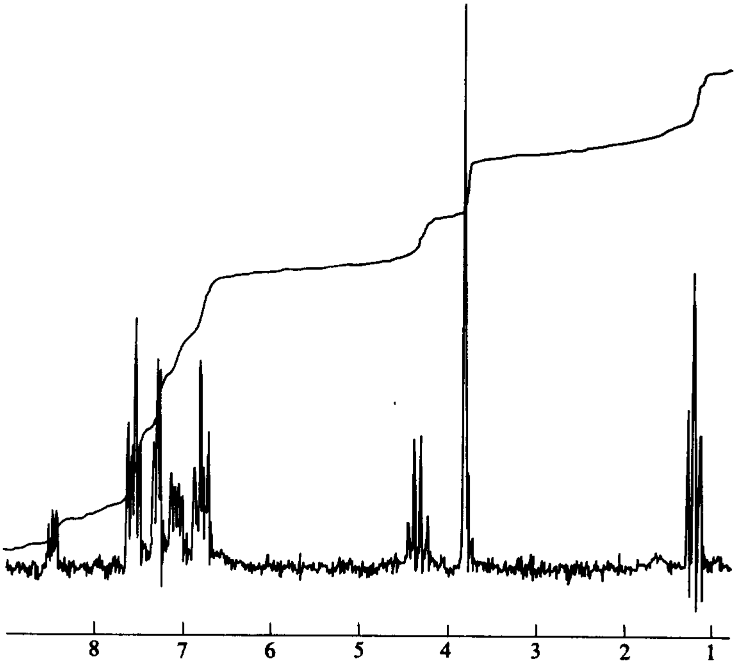
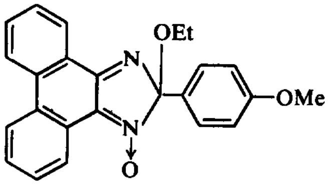


Fig 3. NMR spectrum of compound B in $CDCl_3$.



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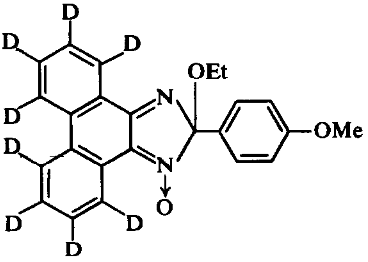

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Compound B seemed to be the autooxidation product from a possible intermediate, 2-ethoxy-2-(4-methoxyphenyl)-phenanthro[9,10-*d*]2H-imidazole.

The oxidation of anisylphenanthro-imidazole 1 (X = OMe) yielded two compounds C and D which also exhibited photochromism but did not show thermochromism in either the solid state or in solution. The elemental analyses and the molecular peaks of the mass spectra agreed with the molecular formula, $C_{23}H_{18}N_2O_2$ for both compounds C and D.

Structure of compound C. The UV spectrum of C showed absorption maxima at 264 (log ε: 3·52), 272 (3·55) and 323 (2·76) nm. These absorptions were shifted to longer wavelength than those of **6**. This spectrum showed the absence of imidazolyl and 4H-imidazolyl groups in compound C.

The NMR spectrum (Fig 4) of C in $CDCl_3$ indicated OMe protons of the anisyl group at

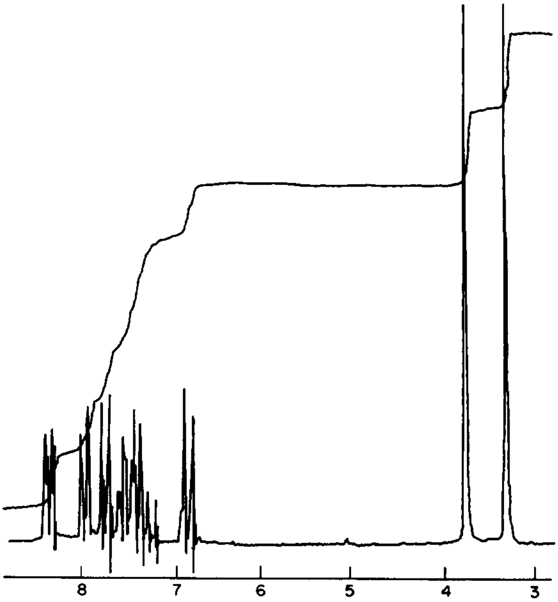
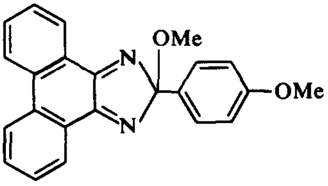


Fig 4. NMR spectrum of compound C in $CDCl_3$.

3·8 (3H, s) and the other OMe protons at 3·35 (3H, s) ppm. The aromatic protons of the *p*-anisyl group were observed at 6·90 (2H, d, $J = 9$ Hz) and 7·85 (2H, d, $J = 9$ Hz) ppm as a pair of doublets. These signals were shifted up-field compared to those of **6**, indicating that the *p*-anisyl group of C was bonded to a saturated C atom in the phenanthreno imidazolyl skeleton. Signals at 8·45 (2H, dd, $J = 8$ Hz), 8·05 (2H, dd, $J = 8$ Hz), and a multiplet between 7·3 and 7·65 (4H, m) ppm were assigned as phenanthreno protons. From these spectral properties structure **10** was deduced for compound C.



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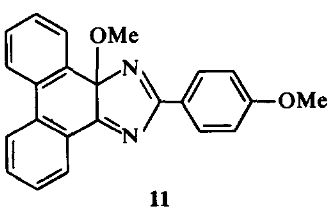
Structure of compound D. This compound showed the same UV spectrum as that of compound A. The NMR spectrum showed a striking resemblance in many of its features to that of compound A, and exhibited aromatic protons of the *p*-anisyl group at 7·05 (2H, d, $J = 9$ Hz) and 8·45 (2H, d, $J = 9$ Hz), the OMe group of *p*-anisyl at 3·88, and phenanthreno protons at 7·25–8·00 ppm. There was however a significant difference between the two spectra; whereas the OEt protons of A appeared at 1·00 and 3·30 as ABX_3, the corresponding signals were replaced by an OMe singlet at 3·15 (3H, s) in D. These spectral properties indicated structure **11** for compound D.



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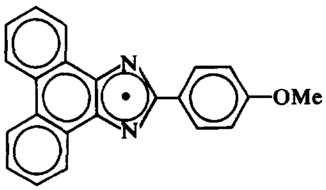
When a mixture of t-butanol and tetrahydrofuran was used as a solvent, the ferricyanide oxidation of anisylphenanthro-imidazole did not afford the corresponding t-butoxyl compound but yielded blue precipitates consisting of radical **12** and its dimer **13**. The benzene solution of the precipitates exhibited thermochromic properties. Thus, the product showed a strong ESR signal both in solid state and in solution.

The longest wavelength absorption maximum was observed at 655 nm in benzene. When a benzene solution was heated, the absorption intensity at 655 nm was enhanced with the rise of temperature. On cooling, the absorbance of the band decreased.



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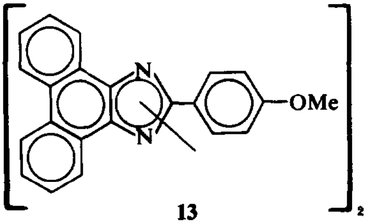

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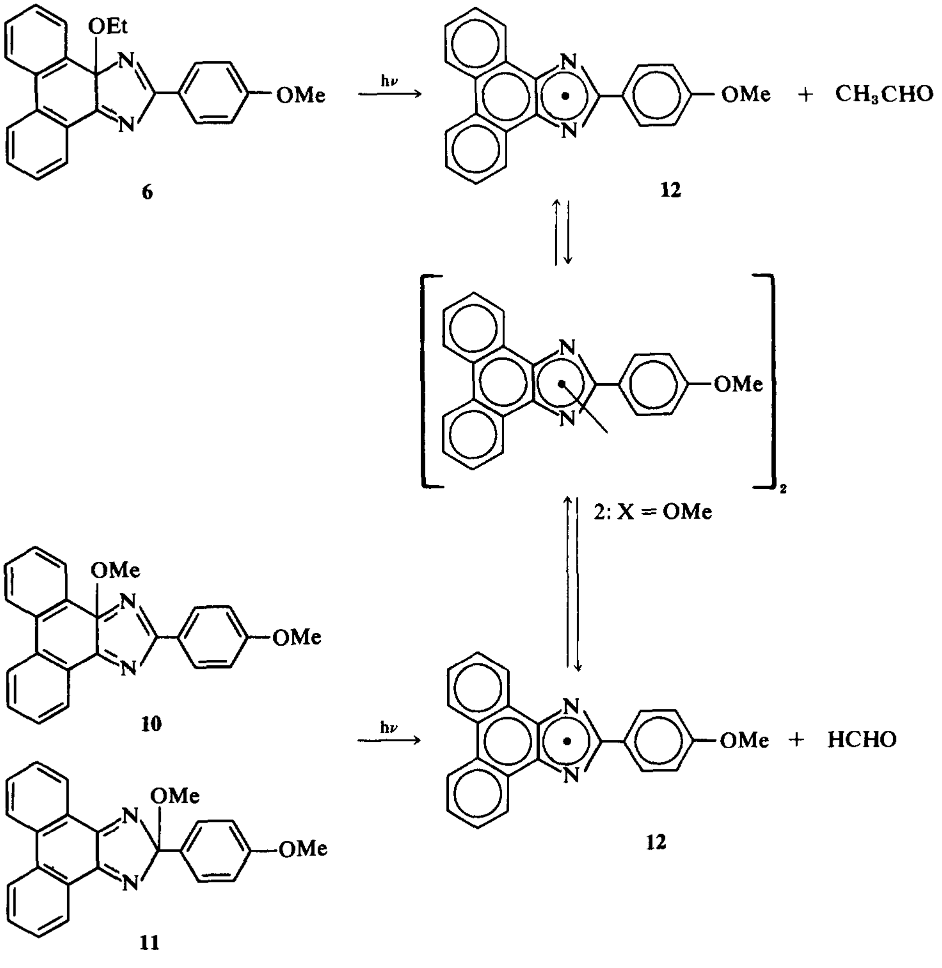
Isosbestic points were observed at 355 and 451 nm with change of temperature from 4° to 26°. These facts suggested that the product was a dimer which dissociated on heating to the free radical responsible for the color observed. If the dimer-monomer equilibrium exists in the benzene solution, a graph of $C\epsilon$ at λ_{max} 655 nm against $1/\epsilon$ should give a straight line of slope KE_m^2 and intercept $KE_m/2$ from the equation, $C\epsilon = KE_m^2\,(1/\epsilon) - KE_m/2$.[9]

In this equation C is the concentration of the dimer taken, ϵ the apparent molar extinction coefficient of the radical, E_m the molar extinction coefficient of the radical and K the equilibrium constant. Since there is a satisfactory linear relation between $C\epsilon$ and $1/\epsilon$, and the assumption of the dimer-monomer equilibrium is satisfied.

Mechanism of photochromism. A pale yellow solution of compound **6** turned to green on exposure to sunlight at room temperature, and the color gradually faded when it was left in the dark. The pale yellow benzene solution which was prepared in the dark gave no ESR signal, whereas the green solution colored by light irradiation showed a marked ESR signal, and the signal intensity gradually decreased on standing in the dark. The same ESR signal was observed with the benzene solution of a compound prepared by Zimmermann's method[10] from a sodio derivative of anisylphenanthro-imidazole **1** (X = OMe) by treating with a half equivalent of bromine and expected to have the structure **13**. This indicated that the OEt group did not associate to the stable radical formed from compound **6**. The OEt and OMe attached to the imidazole nucleus of **6**, **10** and **11** seemed to be removed by light irradiation, because acetaldehyde and formaldehyde were detected as 2,4-dinitrophenyl hydrazones from the colored solutions, respectively.

The intensity of the absorption maximum at 655 nm increased with the first-order rate by irradiation and decreased with obeying the second-order rate law in the dark. The decolorized solution showed thermochromism in a benzene solution. The same ESR signal and the same absorption spectrum as those of irradiated **6** were observed in the warmed benzene solution. Therefore the dimer probably dissociated to a radical on heating the solution. A mechanism for the photochromism is as follows:



EXPERIMENTAL

Spectra were determined on spectrophotometers as follows. UV: Hitachi EPS-3T, IR: Hitachi EPI-S$_2$, NMR: Varian HA-100 JEOL MH-100, ^{13}C-NMR: JEOL PFT-100 (CS$_2$ as standard), Mass: JEOL JES-ME-3X, ESR: JEOL-ME-3X.

2-(4-*Methoxyphenyl*)-*phenanthro*[9,10-d]*imidazole* (**1**, X = OMe). This compound was prepared by the method described[5] as colorless needles, m.p. 255–256°, lit.[11] 255–256°.

2-(4-*Methoxyphenyl*)-*octadeuterophenanthro*[9,10-d] *imidazole*. This compound was prepared by the same method as in compound **1** (X = OMe) except that octadeuterophenanthrenequinone was used instead of phenanthrenequinone, m.p. 255°; Molecular peak (*m*/*e*) of mass spectrum: 332·1768 (Calcd. for $C_{22}H_8D_8N_2O$: 332·1764)

Preparation of 2-(4-*methoxyphenyl*)-4-*ethoxyphenanthro*[9,10-d]4H-*imidazole* (**6**) *and* 2-(4-*methoxyphenyl*)-2-*ethoxyphenanthro*[9,10-d]2H-*imidazole* N-*oxide* (**8**). A cold 10% aqueous soln of potassium ferricyanide (200 ml) was added slowly to a soln of **1** (X = OMe) (1·0 g) dissolved in 99% EtOH (100 ml) containing KOH (6 g). During the addition the mixture was maintained at 5° to 10° and vigorously stirred under the stream of O$_2$. A deep blue color first appeared in the soln and then a light green ppt separated. After the addition was complete (2·0 hr) the ppt was collected by suction filtration, washed with water repeatedly and dried. The ppt was washed with cold EtOH, and the residue was dissolved in benzene. Undissolved material was removed by filtration, and to the filtrate n-hexane was added to give 200 mg of light yellow prisms, m.p. 175–176°. (Found: C, 78·06; H, 5·62; N, 7·67. Calcd. for $C_{24}H_{20}N_2O_2$: C, 78·23; H, 5·48; N, 7·65%; Molecular peak (*m*/*e*) of mass spectrum: 368·153065 (Calcd. for $C_{24}H_{20}N_2O_2$: 368·152469). Molecular weight of **6** was determined to be 360 in toluene at 37° by the VPO method.

The filtrate separated from **6** was concentrated until a crystalline substance **8** separated. This was recrystallized twice from benzene-hexane to give colorless needles, m.p. 176°. This substance showed neither photochromic nor thermochromic properties. The molecular peak in the mass spectrum was *m/e* 384·1457 (Calcd. for $C_{24}H_{20}N_2O_3$ 384·1473; Found: C, 75·11; H, 5·09; N, 7·36. Calcd. for $C_{24}H_{20}N_2O_3$: C, 74·97; H, 5·25; N, 7·29%).

Oxidation of 2-(4-*methoxyphenyl*)-*octadeuterophenanthro*[9,10-d]*imidazole*; **7** *and* **9**. Octadeutero compounds **7** and **9** were prepared by the same method as used for **6** and **8**, m.p. 175° and 176°, respectively. Molecular peaks (*m/e*) of mass spectra of **7** and **9**: 376·2047, 392·2036 (Calcd. for $C_{24}H_{12}D_8N_2O_2$, $C_{24}H_{12}D_8N_2O_3$: 376·2026, 392·2020), respectively.

Preparation of 2-(4-*methoxyphenyl*)-4-*methoxy-phenanthro*[9,10-d]4H- (**11**) *and* 2-(4-*methoxyphenyl*)-2-*methoxy-phenanthro*[9,10-d]2H-*imidazoles* (**10**). A cold 10% aqueous soln of potassium ferricyanide (200 ml) was added to a soln of **1** (X = OMe) (1 g) dissolved in 99% MeOH (100 ml) containing KOH (6·0 g). During the addition the mixture was maintained at 7° and vigorously stirred under the stream of N_2 instead of O_2. After the addition was complete (2·0 hr) a light green ppt was collected by suction filtration, washed with water repeatedly and dried. The ppt was dissolved in benzene-hexane, and left for 2 days to give unidentified colorless crystals. Evaporation of the filtrate gave a yellow oil which crystallized on the addition of EtOH. The yellow crystalline material was recrystallized from EtOH to yield light yellow prisms (91 mg) of **11**, m.p. 150–151°; Molecular peak of mass spectrum *m/e* 354·1385 (Calcd. for $C_{23}H_{18}N_2O_2$: 354·1370; Found: C, 77·85; H, 5·17; N, 7·89. Calcd. for $C_{23}H_{18}N_2O_2$: C, 77·94; H, 5·13; N, 7·91%).

An ethanol soln prepared from **11** was left in the dark at 5° for 10 days, when large yellow prisms **10** separated, 150 mg, m.p. 207–208°; Molecular peak of mass spectrum *m/e* 354 (Calcd. for $C_{23}H_{18}N_2O_2$: 354; Found: C, 77·87; H, 5·15; N, 8·13. Calcd. for $C_{23}H_{18}N_2O_2$: C, 77·94; H, 5·13; N, 7·91%).

Detection of acetaldehyde and formaldehyde from irradiated solutions of **6**, **10** *and* **11**. Solns of 300 mg of **6**, **10** and **11** in 100 ml benzene were respectively irradiated with high pressure mercury lamp (500 w) under N_2. The N_2 stream was conducted into a 1 N HCl soln of 2,4-dinitrophenylhydrazine to detect an aldehyde. From compound **6**, 2,4-dinitrophenylhydrazone of acetaldehyde was obtained as orange-red needles, m.p. 146–146·5°, and the hydrazone of formaldehyde was obtained as yellow needles, m.p. 166°, from compounds **10** and **11**.

Oxidation product of 2-(4-*methoxyphenyl*)-*phenanthro*[9,10-d]*imidazole* (**1**, X = OMe) *in t-butanol*. To a soln of **1** (X = OMe; 1 g) in a mixed solvent of THF (50 ml) and t-BuOH (50 ml) containing 1 N KOH (50 ml) about 400 ml of 10% KOH was gradually added during 1·5 hr with stirring in the stream of O_2 at 5°. A deep blue color appeared and a deep blue ppt separated. The ppt was collected, washed with water and dried *in vacuo*, to yield about 1 g of the compound, m.p. 142–146°. (Found: C, 81·37; H, 4·89; N, 8·63. Calcd. for $C_{44}H_{30}N_4O_2$ (bis(2-(4-methoxyphenyl)phenanthro-[9,10-d]imidazolyl): C, 81·70; H, 4·68; N, 8·66%).

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