

Structure of the Chromotropic Dimers produced from 2-Arylphenanthro[9,10-*d*]imidazoles

By Yoshiko Sakaino, Department of Chemistry, Faculty of Education, Gunma University, Maebashi, Japan
Hiroshi Kakisawa* and Takenori Kusumi, Department of Chemistry, Tokyo Kyoiku University, Otsuka, Tokyo, Japan

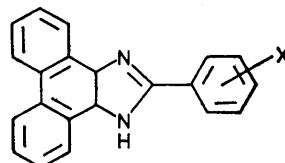
The dimer produced from 2-phenylphenanthro[9,10-*d*]imidazole by oxidation with hexacyanoferrate(III) is shown to be 2,2'-diphenyl-1*H*,2'*H*-1,2'-biphenanthro[9,10-*d*]imidazolyl (23). Derivatives of this dimer substituted in the phenyl rings have been obtained similarly, and their chromotropic properties are reported.

MANY organic compounds change colour reversibly on irradiation (photochromism), heating (thermochromism), or trituration (piezochromism). Hayashi and Maeda have reported that oxidation of 2,4,5-triphenylimidazole affords dimeric products which show these chromotropic properties owing to reversible dissociation to the coloured 2,4,5-triphenylimidazolyl radical.¹ We have found previously that u.v. irradiation of 2,4,5-triphenylimidazole in ethanol brings about dehydrocyclization, affording 2-phenylphenanthro[9,10-*d*]imidazole (1).² This was expected to have interesting chromotropic properties because of the planarity of the molecule and the extended conjugation. Oxidation of various substituted 2-phenylphenanthro[9,10-*d*]imidazoles with hexacyanoferrate(III) in ethanolic potassium hydroxide afforded compounds which exhibited a reversible colour change on heating or trituration, but which did not show any photochromism either in solution or in the solid state.† Zimmermann has synthesized a dimer of 2-phenylphenanthro[9,10-*d*]imidazole by oxidation of the sodium salt with bromine, but did not report its structure and properties.⁴

We describe here the preparation and identification of dimers from various phenylphenanthroimidazoles, and their chromotropic properties.

Preparation of Dimers.—When an aqueous solution of potassium hexacyanoferrate(III) was added to a solution of 2-phenylphenanthroimidazole (1) in ethanolic potassium hydroxide, a purple colour appeared, and a greenish yellow precipitate gradually separated. The purified crystalline product showed thermo- and piezo-chromic properties, but no colour change was observed upon irradiation. Various derivatives, (2)—(9), of 2-phenylphenanthroimidazole were oxidized by the same method to obtain the corresponding dimers (11)—(18). However oxidation of 2-(*p*-nitrophenyl)phenanthroimidazole did not afford the corresponding dimer. The absorption spectrum of 2-(*p*-nitrophenyl)phenanthroimidazole showed maxima at 251sh, 258, 284sh, 303sh, and 399 nm in ethanol, markedly shifted to longer wavelengths [261, 271, 300sh, 325sh, and 461 nm] in ethanolic potas-

sium hydroxide. This red shift suggests the formation of an anion (19) whose charge is extensively delocalized.



- | | |
|-----------------------------------|-----------------------------------|
| (1) X = H | (6) X = <i>o</i> -OMe |
| (2) X = <i>p</i> -Me | (7) X = <i>o</i> -Me |
| (3) X = <i>p</i> -Cl | (8) X = <i>o</i> -Cl |
| (4) X = <i>m</i> -Cl | (9) X = <i>o</i> -NO ₂ |
| (5) X = <i>m</i> -NO ₂ | |

Compounds (10)—(18) are the dimers from compounds (1)—(9), respectively

The facts that the oxidation is conducted under alkaline conditions and that the transient blue colour gradually fades to afford a yellowish precipitate imply that the dimers are produced from phenanthroimidazole anions by way of phenanthroimidazolyl radicals. The resistance of 2-(*p*-nitrophenyl)phenanthroimidazole to oxidation is probably due to the unusual stability of its anion (19).

Analytical molecular weight data (from high resolution mass spectra) for the oxidation products ‡ show that they are dimers of the corresponding phenanthroimidazoles. Thus, whereas oxidation of monophenylimidazoles gives neither the corresponding radical nor the dimer and diphenylimidazoles give the corresponding radicals only in small amounts,^{1f} 2,4,5-triphenylimidazole and 2-arylphenanthroimidazoles give dimers in good yields. 2-Arylpyreno[9,10-*d*]imidazoles did not afford dimers.

Structure of Dimers.—Zimmermann proposed a hydrazino structure (20) for the thermochromic dimer from 2-phenylphenanthro[9,10-*d*]imidazole (1) on the basis of the similarity of its properties to those of the oxidation product of 2,4,5-triphenylimidazole, but n.m.r. and u.v. spectra suggested that this was incorrect. The u.v. spectrum showed maxima at 217sh, 233, 253sh, 261, 271, 287sh, 298, 314, 329, 346sh, 364, 391sh, and 580 nm in hexane. The intensity of the maximum at 580 nm was enhanced by an increase in the temperature and weakened upon cooling; this maximum was therefore assigned

¹ T. Hayashi and K. Maeda, *Bull. Chem. Soc. Japan*, (a) 1960, **33**, 565; (b) 1962, **35**, 2057; (c) T. Hayashi, K. Maeda, and M. Moriga, *ibid.*, 1964, **37**, 1653; (d) T. Hayashi, K. Maeda, and T. Kanaji, *ibid.*, 1965, **38**, 857; T. Hayashi and K. Maeda, *ibid.*, (e), 1965, **38**, 2202; (f) 1970, **43**, 429.

² Y. Nagai and Y. Sakaino, *Nippon Kagaku Zasshi*, 1969, **90**, 309.

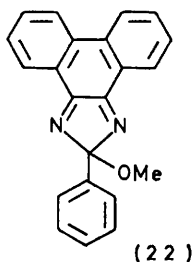
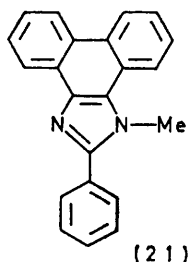
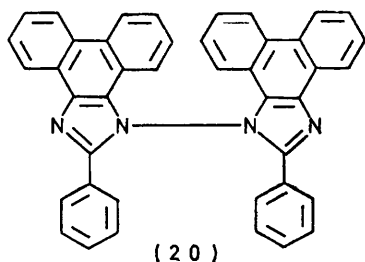
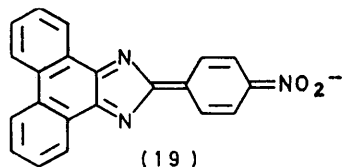
³ Y. Sakaino, H. Kakisawa, K. Arita, M. Kouno, and H. Morishima, *Tetrahedron*, 1973, **29**, 1185.

⁴ H. Baumgärtel and H. Zimmermann, (a) *Z. Naturforsch.*, 1963, **18b**, 406; (b) *Chem. Ber.*, 1966, **99**, 843.

† Oxidation of 2-(*p*-methoxyphenyl)phenanthro[9,10-*d*]imidazole with hexacyanoferrate(III) in ethanolic potassium hydroxide did not give a thermochromic dimer, but instead afforded 4-ethoxy-2-(*p*-methoxyphenyl)-4*H*-phenanthro[9,10-*d*]imidazole, which showed a characteristic colour change on irradiation.³

‡ Available as Supplementary Publication No. SUP 21512 (3 pp.). For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1974, Index issue.

to the 2-phenylphenanthroimidazolyl radical produced by dissociation of the dimer (see later). The u.v.



spectrum of 1-methyl-2-phenylphenanthroimidazole (21) shows maxima at 237, 252, 260, 268, 287, 311, 345, and

seemed to be composed of two chromophoric units: a 1-substituted 2-phenyl-1*H*-phenanthroimidazole, and a 2-substituted 2-phenyl-2*H*-phenanthroimidazole, and the structure (23) was deduced.

This structure was confirmed by the ¹H n.m.r. spectrum (Table 1), which could be analysed by comparison with those of compounds (1), (21), (22), and (24)—(26) and by studying the spectra of the [*phenyl*-²H₁₀]- and [*phenanthro*-²H₁₆]-derivatives of the dimer. The spectrum of the parent imidazole (1) exhibited two low-field double doublets (δ 8.85 and 8.60), assigned to the H-4 and -11 and H-7 and -8, respectively. The coincidence of the signals for each of these pairs of protons shows that the imidazole (1) has a symmetric structure with a proton exchanging between positions 1 and 3. The 1-methyl- (21) and 1-phenyl-2-(*p*-methoxyphenyl)- (24) derivatives also showed four low-field proton signals, but all with different chemical shifts because of the asymmetric structure. On the other hand, the signals of H-4, -11, -7, and -8 in the 2*H*-imidazole (29) appeared at relatively high field, and those of each of the two pairs H-4 and -11 and H-7 and -8 were coincident. In the case of the 3*a*-substituted 3*aH*-phenanthroimidazole (26), the signals of the corresponding four protons also appeared at relatively high field, but all exhibited different chemical shifts. The n.m.r. spectrum of the dimer (23) showed four low field double doublets at δ 9.3, 8.85, 8.68, and 8.68, and two two-proton double doublets at higher field (8.05 and 8.00). This confirmed the structure (23).

The u.v. and n.m.r. spectra of the remaining thermochromic dimers (11)—(18) indicated that they had

TABLE 1

Characteristic ¹H n.m.r. signals of phenanthroimidazole derivatives in CDCl₃ (δ values: *J*/Hz in parentheses)

Compd.	Position: 4(4')	11(11')	7(7')	8(8')	5,6,9,10 (5',6',9',10')	2'',6'' (2'',6'')	3'',5'' (3'',5'')	Other
(1) *	8.85 (dd, 7.0, 2)	8.85 (dd, 7.0, 2)	8.60 (dd, 7.0, 2)	8.60 (dd, 7.0, 2)	7.6 (dt, 2, 7.0)	8.4 (dd, 8.0, 2)	7.5 (3H, m) †	
(21)	8.9—8.5 (m)		7.4—7.7 (m)		8.7 (m)	7.4—7.7 (m)	1-Me: 4.05	
(24)	8.9—8.6 (m)		7.7—7.8 (m)		7.5 (d, 9)	6.8 (d, 9)		
(25)	8.45 (dd, 7.5, 1.8)	8.45 (dd, 7.5, 1.8)	8.05 (dd, 7.5, 1.1)	8.05 (dd, 7.5, 1.1)	7.4 (dt, 7.5, 1.1)	7.85 (d, 9)	6.90	OMe: 3.35(s), 3.79(s)
(26)	8.0—7.3 (m)		8.45		7.05		OMe: 3.15(s)	
(23)	8.85 (dd, 7, 2.5)	9.3 (dd, 7, 2.5)	8.68 (dd, 8, 2)	8.68 (dd, 8, 2)	7.2—7.7 (m)	7.5 (m)	7.1 (3H, m) †	
(16)	8.05 (dd, 6.5, 1)	8.05 (dd, 6.5, 1)	8.0 (dd, 6, 1)	8.0 (dd, 6, 1)	7.2—7.7 (m)			Me: 1.9(s), 2.15(s)
(15)	8.8 (dd, 7.5, 2)	9.3 (dd, 7.5, 2)	8.6 (dd, 8, 2)	8.6 (dd, 8, 2)				OMe: 2.95(s), 3.20 (s)
	8.0 (4H, m)		8.6 (m)		8.6 (m)			

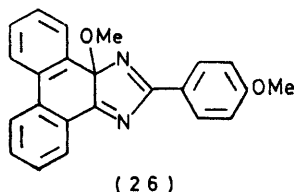
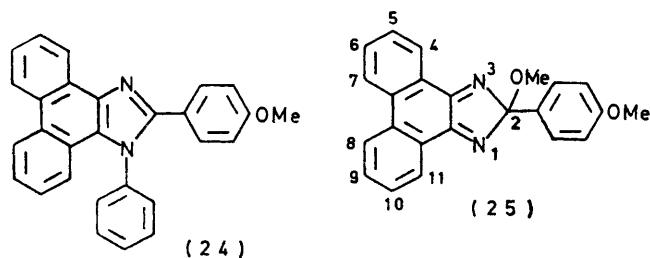
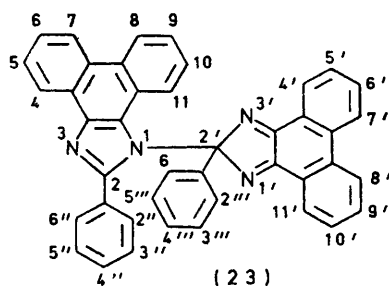
* In (CD₃)₂SO. † 3'', 4'', and 5''-Proton signals.

362 nm. On the other hand, 2-methoxy-2-phenyl-2*H*-phenanthroimidazole (22)⁵ has maxima at 216sh, 225, 231, 254sh, 262, 271, 304, 315, 327, 369, and 388 nm in hexane. All these maxima of compounds (21) and (22) are found in the spectrum of the dimer, and the u.v. spectrum of a 1:1 mixture of (21) and (22) closely resembled that of the dimer except for the absence of a peak at 580 nm in the former. Thus, the dimer molecule

structures similar to that of the dimer (23). Signals for the two methoxy-groups of the dimer (15) and the two methyl groups of the dimer (16) are shifted upfield by an anisotropic effect of the neighbouring aryl groups. The same effect is observed in the *N*-phenylimidazole (24); the 2- and 6-protons of the *p*-methoxyphenyl group resonate at δ 7.5, whereas the corresponding two protons

⁵ Y. Sakaino *et al.*, in preparation.

in the 3a-methoxy-3aH-phenanthroimidazole (26) resonate downfield, at δ 8.45.



Properties of Dimers.—The colour-change phenomena observed with the dimers (10)—(18) upon heating, trituration, and irradiation are summarized in Table 2. The

dimers (10)—(18) dissolved in benzene: the solutions turned blue when heated and the colour faded on cooling.

The e.s.r. spectrum of the yellow crystals of the dimer (10) showed no signal at room temperature, but a weak signal with a single peak (g 2.0025) began to appear above 40 °C, accompanied by the development of colour, the intensity of which was rapidly increased above 90 °C and decreased on cooling. This behaviour suggests a dissociation to a coloured radical on warming.

Table 2 shows the u.v. absorption maxima of the radicals produced from the dimers (10)—(18). Electron-donating substituents (OMe and Me) on the phenyl group cause a hypsochromic shift of the longest-wavelength band whereas electron-accepting substituents (*o*-NO₂ and *m*-NO₂) cause a bathochromic shift. The reversibility of the dissociation of the dimers into radicals upon heating was established by spectroscopic measurements. The colour-change phenomena on heating the dimers in benzene were recorded as changes in the absorption spectra in the visible region. The existence of isobestic points showed that the formation of radicals is reversible.

The dimer-radical equilibrium constants were calculated by means of the equation:³ $C\epsilon = (K\epsilon_m)^2(1/\epsilon) - K\epsilon_m/2$, where ϵ is the apparent molar extinction coefficient at the longest wavelength absorption maximum, ϵ_m the molar extinction coefficient of the radical, C the initial concentration of dimer, and K the equilibrium constant. The existence of a satisfactory linear relation between $C\epsilon$ and $1/\epsilon$ supports the assumption of reversibility of the dimer-radical equilibrium. The dissociation constants, K , calculated from the slope and the intercept of the line, and the enthalpy changes, ΔH , are listed in Table 2. The order of substituents promoting dissociation was *p*-Me > *p*-H > *p*-Cl. Elec-

TABLE 2
Reversible colour changes of 2,2'-diarylphenanthro-[9,10-*d*]imidazolyls on irradiation (p), heating (t), and trituration (pie)

Compd.	X	M.p. (°C)	Chromotropism			Colour change	$\lambda_{\max.}/\text{nm}$	$-\log K$	$\Delta H/$ kcal mol ⁻¹
			Solid	Solution					
(10)	<i>p</i> -H	200—203	pie, t	-70 °C	Room temp.	Yellow → Blue	585	4.17 *	16.90
(11)	<i>p</i> -Me	170—173	pie, t	p	t	Yellow → Blue	617	3.48 *	13.10
(12)	<i>p</i> -Cl	172—180	pie, t	p	t	Yellow → Blue	605	4.30 *	14.13
(13)	<i>m</i> -Cl	188—192	pie, t	p	t	Yellow → Blue	587	4.80 *	16.10
(14)	<i>m</i> -NO ₂	233—235	pie, t	p	t	Yellow → Purple	570	5.40 *	17.79
(15)	<i>o</i> -OMe	176—180	pie, t		t	Yellow → Green	617	6.74 †	
(16)	<i>o</i> -Me	182—185	pie, t		t	Yellow → Blue	602	6.33 †	
(17)	<i>o</i> -Cl	210—215	pie, t		t	Yellow → Purple	580	8.52 †	
(18)	<i>o</i> -NO ₂	222—227	pie, t		t	Yellow → Reddish purple	578	6.48 †	

* Determined spectroscopically. † Determined by e.s.r. The degree of dissociation of compounds (15)—(18) could not be obtained from absorption spectra because of lack of sufficient material.

yellow crystals of the dimer (10) [≡ (23)] turned deep blue when ground in a mortar at room temperature; the colour had faded after several days at 5 °C. When the yellow crystals of the dimer (10) were heated, a purple colour appeared above 40 °C; the colour was enhanced by a further increase in temperature. The same thermochromic behaviour was observed with the

tron-donating substituents at the *para*-position in the phenyl group favoured dissociation. Dissociation decreased in the order *p*-> *m*-> *o*-substituted dimers.

EXPERIMENTAL

U.v. spectra were recorded with a Hitachi EPS-3T spectrophotometer, with a Komatsu CTE and CTR cooling

circulator, and i.r. spectra with a Hitachi EPI-S₂ spectrophotometer. N.m.r. spectra were measured with a Varian HA-100 instrument with Me₄Si as internal standard, and mass spectra with a JES-ME-3X spectrometer.

Materials. The 2-arylphenanthro[9,10-*d*]imidazoles used were synthesized by refluxing phenanthrenequinone (0.02 mol) with the appropriate aldehyde (0.02 mol) and ammonium acetate (0.4 mol) in glacial acetic acid (300 ml) for 2 h. The mixture was then poured into ice-water, and the precipitate was collected and recrystallized from pyridine, methanol, or acetone.^{6,7}

2-[²H₅]Phenylphenanthro[9,10-*d*]imidazole. This was prepared from [²H₅]benzaldehyde, by the same method as used for 2-phenylphenanthro[9,10-*d*]imidazole;⁷ m.p. 312—314°, *M*⁺ 299 (C₂₁H₉N₂D₅).

2-Phenyl[²H₈]phenanthro[9,10-*d*]imidazole. This was similarly prepared from [²H₈]phenanthrenequinone; m.p. 312—314°, *M*⁺ 302 (C₂₁H₆N₂D₈).

2,2'-Diaryl-1H,2'H-biphenanthro[9,10-*d*]imidazolyls (11)–(18).—A cold, saturated aqueous solution of potassium hexacyanoferrate(III) (200 ml) was dropped during 2 h into a solution of 2-(*o*-chlorophenyl)phenanthro[9,10-*d*]imidazole (1 g) in 99% ethanol (100 ml) containing potassium hydroxide (12 g). The mixture was maintained between 5–10°C

and was stirred by bubbling in a stream of oxygen. The precipitate was collected, washed with water, and dried. The crude product (0.98 g) was dissolved in benzene and the solution was filtered and concentrated; addition of hexane afforded the dimer as yellow *prisms*, m.p. 210—215° (95%). Other dimers were prepared similarly, giving yellow *prisms* except for (15), which is orange; yields: (11), 35%; (12), 45%; (13), 40%; (14), 45%; (15), 80%; (16), 80%; (18), 90%.

Deuteriated dimers were prepared similarly, from the foregoing deuteriated compounds.

N-Methylation⁸ of 2-Phenylphenanthro[9,10-*d*]imidazole.—A mixture of 2-phenylphenanthroimidazole (450 mg) and potassium (78 mg) in anhydrous dioxan (100 ml) was refluxed for 3 h, cooled, treated with methyl iodide (284 mg), warmed for 0.5 h, and then refluxed for 2 h. The precipitate was filtered off and washed with ethanol. The filtrate was evaporated to dryness, and the residue was washed with sodium thiosulphate solution. The residue and the precipitate were combined and recrystallized from acetone-water to give colourless *needles* (161 mg), m.p. 185—186° (Found: C, 85.45; H, 5.1; N, 9.1. C₂₂H₁₆N₂ requires C, 85.65; H, 5.25; N, 9.1%).

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⁶ Y. Sakaino, *Nippon Kagaku Zasshi*, 1971, **92**, 366.

⁷ E. A. Steck and A. R. Day, *J. Amer. Chem. Soc.*, 1943, **65**, 455.

⁸ P. G. Haines and E. C. Wagner, *J. Amer. Chem. Soc.*, 1949, **71**, 2793.