TRIARYLIMIDAZOLE RADICALS AND THEIR DIMERS (REVIEW)

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Despite the fact that 2,4,5-triarylimidazoles have long been known [1] and have always been attractive to investigators as subjects for the study of chemiluminescence, it was only in 1960 that it was found that stable free radicals are formed during their oxidation and that the radicals form dimers in the crystalline state that have piezo-, photo-, and thermochromic properties. The aim of the present review is a correlation of the known information on the chemistry of stable radicals of the triarylimidazolyl series.

The possibility of the existence of a triarylimidazolyl radical was first predicted by Kautsky and Kaizer [2] who supposed that the chemiluminescence of lophine (2,4,5-triphenylimidazole), which is observed during its oxidation in strongly alkaline media, is due to the interaction of the free radical (triphenylimidazolyl) formed under these conditions with the base.

In an investigation of the mechanism of the chemiluminescence of lophine, Hayashi and Maeda [3] isolated a new phototropic substance, which was crystallized from ethanol as lemon-yellow needles and gave colorless or slightly yellow solutions in organic solvents. When these solutions were irradiated with sunlight or a mercury lamp or were heated, they acquired a red-violet color that gradually vanished when the irradiation or heating was discontinued. Hayashi and Maeda [4] demonstrated that the red-violet color of the solution is due to the presence of free radicals (I); this is confirmed by the ESR spectra, which contain a singlet with a width of 7.3 G and a g factor of 2.003.



Subsequent investigations demonstrated that the product of the oxidation of triphenylimidazole that was isolated by Hayashi and Maeda [3] is the dimer of the triphenylimidazolyl radical [5-7].

Methods for the Synthesis of Triphenylimidazolyl

Radicals and Their Dimers

The simplest method for the synthesis of triarylimidazolyl dimers is the method used by Hayashi and Maeda and consists in the fact that the triphenylimidazole, dissolved in aqueous alcoholic alkali, was oxidized by the addition of an aqueous solution of potassium ferricyanide while stirring the solution with a stream of oxygen. The oxidation of the imidazole proceeds practically identically when either oxygen or nitrogen is bubbled into the reaction medium or even simply in the air [9].

After separation and washing with water, the product that precipitates from the solution during oxidation is a bright-violet finely crystalline substance that has weak paramagnetic susceptibility; the product loses its color on storage. A bright-violet coloration develops when it is triturated with or dissolved in most organic solvents, and a strong ESR signal is observed. This form of the dimer is called the piezochromic form. It can also be obtained by oxidation of triarylimidazoles with bromine in aqueous alco-

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• 1974 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00. TABLE 1. UV and Visible Absorption Spectra of Dimers Obtained from Lophine and Its Derivatives [10]



R	,dimer (before irradiation)	radical obtained the dimer	by irradiation of	Radical-solution color
Phenyl	271 (T), 266 (E)	349 (T), 347 (E) 364 (B), 359 (T)	555 (T), 560 (E)	Red-violet
p-Tolyl	269 (E)	360 (T), 364 (B)	575 (B), 575 (T)	Violet
p-Chlorophenyl	266 (T)		570 (T), 570 (B)	Violet
3,4-Methylenedioxyphenyl	317 (T), 312 (E)	390 (B)	690 (B)	Yellow-green
3,4-Dimethoxyphenyl	293 (T), 302 (E)	395 (B)	700 (B)	Blue-green
o-Tolyl	267 (E)	351 (T), 354 (B)	565 (T), 565 (B)	Violet
o-Methoxyphenyl	(291 (E)		6 2 0 (B)	Blue
a-Naphthyl	277 (E)	445, 473 (B)	750 (B)	Green
p-Methoxyphenyl	295 (E), 302 (T)	385 (E), 390 (B)	620 (E), 605 (B)	Blue
p-Bromophenyl	279 (E), 283 (T)	367 (E), 375 (B)	580 (E), 573 (B)	Red-violet
m-Chlorophenyl	283 (T)	349 (B)	565 (B)	Red-violet
o-Chlorophenyl		345 (B)	558 (B)	Red-violet
3,4-Diethoxyphenyl	[395 (B)	710 (B)	Green
4-Diphenylyl	261 (E)	402 (E)	610 (E)	Blue-green

*Abbreviations: T is tetrahydrofuran, E is ethanol, and B is benzene.

hol solution [8]. The piezochromic form of the dimers is unstable and decomposes instantaneously in solutions to give radicals, which dimerize to form another more stable form called the thermochromic or photochromic form of the dimers, which was also isolated by Hayashi and Maeda.

Diverse dimers of triarylimidazoles that have substituted phenyl rings [10, 11] and residues of polycyclic hydrocarbons (diphenylyl [12] and α - and β -naphthyls [13]) as substituents can be obtained by oxidation of the triarylimidazoles with potassium ferricyanide.

The reaction of the potassium or sodium salt of a triarylimidazole with iodine or bromine in ether solution [5, 7, 14] can also be used for the synthesis of the dimers. This method was used to obtain a number of dimers having different substituents in the phenyl rings, including bis(2-phenyl-4,5,9,10-phenanthroimidazolyl) (II). The presence of a p-nitro group in the phenyl ring makes it impossible to obtain the corresponding dimer by this method, since the nitro compound forms a red-violet salt (III) with alkali metals that does not react with halogen in the expected manner [14].

The presence of a p-dimethylamino group also leads to complications in the preparation of the corresponding dimers because of the reaction of the resulting radical with halogen to form salt IV.



III $R = C_6H_5$, $C_6H_4NO_2 - p$; $CH_3 = K$, Na; IV $R = C_6H_5$, $C_6H_4N(CH_3)_2 - p$

In the oxidation of triarylimidazoles in benzene solutions with lead dioxide, the yield of radicals usually does not exceed 5-10%, except for 2,4,5-tris(p-dimethylaminophenyl)imidazole, which is converted to a dimer in quantitative yield under these conditions.

Replacement of one of the phenyl rings with a furan [15] or thiophene [16] residue leads to a sharp change in the capacity for the formation of free radicals. When they are oxidized by both lead dioxide and

Spin density	Position								al
	0	n	0'	u	1	2	3	4	Tot spin den
Observed MO method ρ_{obs}/ρ_{cal} ρ_{corr}	0,156 0,053 2,9 0,159	0,156 0,062 2,5 0,186	0,130 0,036 3,6 0,108	-0,078 0,002 39 -0,060	0,018 0,540	0,170 0,510	0,114 -0,342	0,012 -0,360	1,050 0,972 0,936

TABLE 2. Observed and Calculated Spin Densities of theTriphenylimidazolyl Radical [17]

potassium ferricyanide, the resulting radicals polymerize to form paramagnetic polymers that are capable of retaining their paramagnetic susceptibility in the crystalline state for a year [15, 16].

Spectra of Triarylimidazolyl Radicals and Their Dimers

in the UV and Visible Regions

The UV spectra of solutions of the dimers usually have one maximum at 267-317 nm, depending on the solvent and the substituents in the phenyl rings (Table 1). The absorption band of the dimer weakens when solutions of the dimers are irradiated with sunlight or UV light, and two absorption bands of the radical develop at 347-473 and 550-750 nm. The introduction of any substituent except the nitro group into the phenyl ring causes a shift in the absorption maximum to the long-wave region. The presence of a nitro group shifts the absorption maximum to the short-wave region or leaves it unchanged as compared with the unsubstituted derivative [12].

ESR Spectrum of the Triphenylimidazolyl Radical

Ueda [17] obtained a spectrum with a resolved hyperfine structure for the triphenylimidazolyl radical. Judging from the spectrum, there is no spin density on the nitrogen atoms. The spin density was calculated using the exchange integral h = 1, and the computed spin density on the nitrogen atoms in this case is close to zero. The calculated electron densities are presented in Table 2 [17]. In calculating the spin density it was assumed that the o, p, o', 2, and 3 positions have positive electron densities and that the m, 1, 1', and 4 positions have negative electron densities. The m', p', and N positions were not considered, since there is no experimental splitting for them.



Structure of the Dimers

Two types of dimers – piezochromic and thermochromic – that differ from one another in both properties and structure [9] can be obtained in the oxidation of triphenylimidazole.

On the basis of the absence of an active hydrogen (negative Zerewitinoff test) and the double molecular weight as compared with imidazole, hydrazine-like structure V was proposed for the thermochromic dimer [5-7, 18].



Somewhat later, on comparing the IR spectra of thermochromic dimers [19] (Table 3) with the IR spectra of arylimidazoles and arylisoimidazoles [20], Hayashi and Maeda proposed the hexaphenyl-2,2-di-2H-imidazolyl structure (VI) [19] for the thermochromic dimer. White and Sonnenberg, also on the basis of the IR spectra of the dimers [9], imidazoles, and isoimidazoles, proposed a structure for the pi-ezochromic dimer that coincides with structure VI proposed by Hayashi and Maeda for the thermochromic dimer and structure VII for the thermochromic dimer [9]. The grounds for this assumption were the

TABLE 3. Absorption Bands in the	he IR Spectra of the Dimers
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Dimers	Absorption bands in the IR spectra, cm ⁻¹							
2,4,5-Triphenyl-	1617 sh	1603 s	1577 m	1565 m	1554 s	1526 sh	1501 m	1485 s
2,4,5-Tri-(p-	1622 sh	1604 s	1574 sh	1568 m	1551sh	1520 w	1501 s	
2,4,5-Tri-(p- chlorophenyı)- imidazolyl	1616 sh	1600 s	1572 W	1560 sh	1553m	1519 w	1495sh	1484 s
2-(p-Chlorophenyl)- 4,5-diphenyl- imidazolyl	1618 sh	1624 m	1575 m	1565 m	1556m	1525 sh	1501 m	1484 s
2,4,5 - Triphenyl -	1616 vs	1600 m	1580 vvw		1554 m	1520 vvw	1499m	1487 m
2,4,5-Triphenyl- imidazolyl‡	1626 w	1605 m	1	1562 s				1489 s

* Data from [19].

† Data from [9] for the thermochromic dimer.

‡ Data from [9] for the piezochromic dimer.

TABLE 4. Thermodynamic Data for the Dissociation of Bis(triphenylimidazolyls) into Radicals at 25°C in Toluene [12, 14]



presence in the IR spectrum of the piezochromic dimer of an absorption band at 1562 cm^{-1} close to the band at 1563 cm^{-1} for 2,4,4,5-tetraphenyl-4H-isoimidazole and the presence in the IR spectrum of the thermochromic dimer of a band at 1554 cm^{-1} , which is characteristic for 2H-isoimidazoles, and of bands characteristic for imidazole.



Chemical Properties of Triarylimidazolyl Radicals

Triarylimidazolyl radicals are comparatively stable with respect to air oxygen and are capable of prolonged existence in solution in aprotic solvents. Thus when a solution of the photochromic dimer in carbon tetrachloride is irradiated with a mercury lamp in the presence of oxygen, ~ 20 h was required for conversion of the radical to the peroxide [8]. The radicals react considerably more rapidly with compounds that have an unpaired electron. They instantly add nitric oxide to give a nitroso derivative [8], and they form hydroperoxide VIII [21] with hydrogen peroxide.



The radicals have strong dehydrogenating properties and are capable of instantly stripping off hydrogen from carbazole, diphenylamine, hydroquinone, and α, α -diphenyl- β -picrylhydrazine [22], and they TABLE 5. Thermodynamic Data for the Rate Constants for the Dissociation of Bis(triarylimidazolyls) into Radicals in Toluene Solution



are reduced to triarylimidazoles in the process. The dehydrogenation of ethanol proceeds considerably more slowly [8] in the course of several days during constant irradiation with a mercury lamp.

The piezochromic and thermochromic dimers are quantitatively reduced to imidazoles on reaction with lithium aluminum hydride [9], and they form imidazoles in 50% yield on reaction with hydrochloric or acetic acid; the other products are apparently unstable acetoxy and halo derivatives [9].

Dimer = Radical Equilibrium Constants

The dimers of triarylimidazolyl radicals exist in solution in equilibrium with the radicals. The equilibrium constants for a number of dimers were studied by Zimmermann and Baumgärtel [5, 7, 14]. The dissociation constants were investigated by spectrophotometry using the absorption maximum of the radical in solution. The equilibrium constants and enthalpies and entropies of dissociation are presented in Table 4. As seen from Table 4, the presence of substituents in the phenyl rings of bis(triarylimidazolyl) facilitates dissociation of the dimers, and substituents having strong electron-donor properties, such as the methoxy and dimethylamino groups, play the greatest role. Replacement of the phenyl rings in the 4,5 positions of the imidazole ring by a 9,10-phenanthrenyl group also lowers the enthalpy of dissociation, probably due to the possibility of greater delocalization of the unpaired electron. The assertion of Baum-gärtel and Zimmermann regarding the absence of a correlation between the capacity of the dimers for dissociation and the Hammett σ constants is presently premature in view of the small number of substituents that have been studied.

Dissociation Rate Constants

The rate constants for the dissociation of the dimers into radicals have been studied in greater detail than the equilibrium constants. The reaction of the dimer with α, α -diphenyl- β -picrylhydrazine (X), the rate of which is described by a first-order equation and is independent of the concentration of X, was used to investigate them [22].



The dissociation rate constants, the activation energies, and the preexponential factors of the Arrhenius equation were determined for seven series of dimers. For all of the investigated series it was found that the logarithms of the rate constants are described by the Hammett equation. The results are presented in Table 5. In contrast to the original studies [12, 13, 23-25] in the present review the logarithms of the rate constants were correlated after separation of the inductive and mesomeric components of the Hammett σ constants [26].

As seen from Table 5, the effect of substituents on the rate constant for dissociation of the dimer is described by the Hammett equation in all of the investigated series, but the relative contributions of the inductive and mesomeric components of the substituents to the stabilization of the transition state vary for different series. Thus, while the contribution of the inductive component is not much greater than that of the mesomeric component for bis(2-aryl-4,5-diphenylimidazolyls) (series 1), the mesomeric component prevails for imidazolyls that have polycyclic hydrocarbon residues as substituents; this is particularly distinctly displayed for $2-(\alpha-naphthyl)$ derivatives (series 6).

It should be noted that while the presence of substituents in the phenyl ring in the 4(5) position of the imidazole ring has practically no effect on the rate of dissociation of the dimers (series 2) for triphenylimidazolyls, when polycyclic hydrocarbon residues are present in the 2 position of the imidazole ring (series 4, 6, 7), these substituents begin to have an effect, although it is somewhat less than is observed with substituents in the 2 position.

The activation energy for dissociation for most of the investigated dimers lies at 21-23 kcal/mole, and it becomes low and commensurable with the activation energy for dissociation of hexaphenylethane (17 kcal/mole) only for compounds that have a β -naphthyl group in the 4(5) position and an α -naphthyl group in the 2 position (series 6 and 7).

The fact that, in contrast to the β -naphthyl group, the presence of an α -naphthyl group in the 4(5) position (series 5) does not have a substantial effect on the activation energy as compared with the triphenyl derivatives (series 1) is somewhat strange.

Photochromism of Triarylimidazolyl Dimers

The photochromic properties of triarylimidazolyl dimers, i.e., their capacity for dissociation under the influence of irradiation to give colored radicals, have been the subject of numerous investigations.

In a study of the photochromism of bis(triphenylimidazolyl) in benzene and toluene at low temperatures (up to -196°) [27] it was found that these photochromic solutions behave quite strangely – on sunlight irradiation of a solid solution (at -195°) the color characteristic for the triphenylimidazolyl radical develops, vanishes as the temperature is gradually raised to -70° , and reappears at temperatures above -30° [28].

An investigation of the photochemical processes in solid solutions of bis(triphenylimidazolyl) in alcohol, benzene, and hexane [29] confirmed the data in [27]. It was noted that irradiation of these solutions with light with λ 253.7, 303-313, and 365 nm causes dissociation of the dimer into radicals. When a sample containing radicals is irradiated with light with λ 470-600 nm, the percentage of radicals decreases

Substituents in the tri- arylimidazole radical	Temp., °C	k, liter. mole ⁻¹ .sec ⁻¹	E _a , kcal/mole	A, liter · mole ⁻¹ · sec ⁻¹
2,4,5-Triphenyl	25,3 35,5 46,4	66 103 146	7,4	1,7 • 107
2,4,5Tri(p-tolyl)	27,0 35,0 44,0 57,0	14 22 30 61	9,5	1,1 · 10 ⁸
2,4,5-Tri(p-chlorophenyl)	29,0 35,3 46,0	200 253 354	6,9	1,9 · 10 ⁷
2 -(p-Chlorophenyl)-4,5- diphenyl	16,5 28,0 44,0	62 108 183	7,2	1,7 • 107

TABLE 6.	Thermodynamic Data for the Recombination of
Triarylimi	dazolyl Radicals in Benzene Solution [8]

rapidly, and the starting dimer is reformed. Thus, the character of the photochromic transformations of the triphenylimidazolyl radical depends on the aggregate state of its solution: in a solid solution at -196° the transition of the colored form to the uncolored form is induced by light, while the transition in liquid solutions at room temperature is a dark process [29].

When the irradiated solutions of the dimers in alcohol are thawed, the radical coloration vanishes at -156 to -127° and is regenerated at -20° . The rate of disappearance of the radical is described by a second-order equation (k=60 liter \cdot mole⁻¹ \cdot sec⁻¹) and proves to be even somewhat higher than the rate of recombination of the radicals in benzene solution at room temperature [29]. From all appearances, the radical exists as an unstable dimer from -156 to -20° [29].

The rate of the dark recombination of the radicals in solution has been investigated spectrophotometrically by the ESR method, but the results obtained by different investigators are not in agreement. Thus, Willks and Willis [30] found that the rate of this reaction has an order of 3/2, while other investigators have found that this reaction is second order [18, 29, 31] and that the reaction proceeds twice as fast in cyclohexane as in benzene [29].

The thermodynamic parameters of the dark recombination in benzene were determined for a number of triarylimidazolyl radicals (Table 6) [8].

In an investigation of the rate of recombination of the radicals (from the rate of decrease of the intensity of the ESR signal) in solid samples of piezochromic dimers [8, 32], it was found that this reaction is described by a third-order equation. The reaction rate constants proved to be $2.0 \cdot 10^{-5}$ and $8.9 \cdot 10^{-5}$ cm⁻² · min⁻¹ at 48.0 and 51.5°, respectively [32].

When solid solutions of the dimers are subjected to γ irradiation (at -196°), the dimer decomposes to give the radical and anion [33].



Triarylimidazoles as Stabilizers for Plastics

The capacity of triarylimidazoles to undergo oxidation to give stable free radicals can be used to suppress the thermal oxidative destruction of polymers. A number of imidazole derivatives, including the triaryl derivatives, have proved to be excellent stabilizers for olefins, polyamides, polystyrene, and rubbers [34]. In tests as stabilizers for polypropylene, thienyldiarylimidazoles have shown themselves to be polyfunctional stabilizers that break oxidation chains and decompose hydroperoxides [35].

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