Structures of Three Isomeric Dimers of 2,4,5-Triphenylimidazolyl[1]

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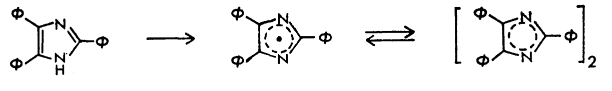
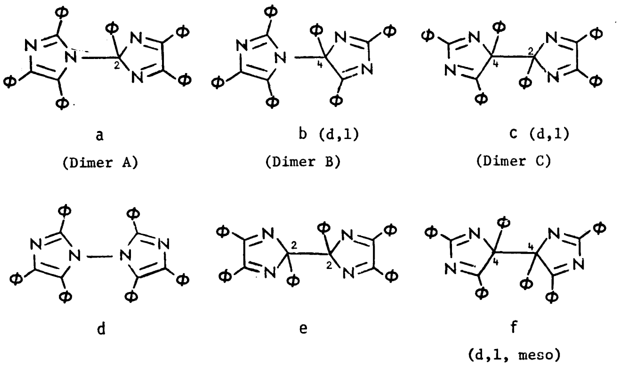
In addition of the piezochromic and the photochromic (dimer A) dimers of 2,4,5-triphenylimidazolyl, two new isomeric dimers were prepared; one (dimer B) being photochromic and the other (dimer C) non-photochromic. Several *p*-substituted derivatives of the dimers were also prepared. By comparison of their NMR and IR spectra, structures (a), (b), and (c) were assigned to the dimers A, B, and C, respectively. On treatment with hydrochloric acid in ethanol, dimer A underwent heterolytic cleavage and gave a mixture of 2-ethoxy-2*H*- and 4-ethoxy-4*H*-2,4,5-triphenylisoimidazole, and 2,4,5-triphenylimidazole.

2,4,5-Triphenylimidazole (lophine) (I) is one of the well-known chemiluminescent substances[2-5] and the recent studies[3-7] on the luminescence mechanism suggested that the lophyl radical is the first intermediate of the luminescence. Another interesting feature of this compound is that it forms on oxidation a photochromic and a piezochromic dimer.[4,8,9] Thus, oxidation of lophine with ferricyanide produces violet lophyl radical which rapidly dimerizes to give the unstable piezochromic dimer. This dimer, when dissolved in benzene, isomerizes rapidly to the photochromic dimer (dimer A) (IA). Photochromism and piezochromism of these dimers have been assumed to be due to the reversible dissociation of these dimers to lophyl radical.[4,8-10]



(I) radical dimer

Although initially the hydrazine structure (d) was suggested *a priori* for the dimer A.[4,11] White and Sonnenberg[9] pointed out the possibility of six dimer structures (a—f)[12] provided that the imidazole rings are linked together, and assigned the structures (f) and (a) for the piezochromic dimer and dimer A, respectively, mainly by comparisons of infrared spectra of these compounds measured in solid states with the model compounds. This assignments, however, would not be considered conclusive and require further confirmation.[13]



Besides these two dimers we have succeeded in preparing further two new dimers; one (dimer B) (IB) is photochromic and the other (dimer C) (IC) is non-photochromic. Thus, piezochromic dimer of I, when refluxed in benzene in the dark, afforded an equilibrium mixture of the three dimers, A, B, and C, which were separated by means of tlc on silica gel. Photochromic dimers, A and B, are interconvertible by UV irradiation, while dimer C is not affected by the light.

While NMR spectrum of the piezochromic dimer could not be measured due to its instability in solutions,

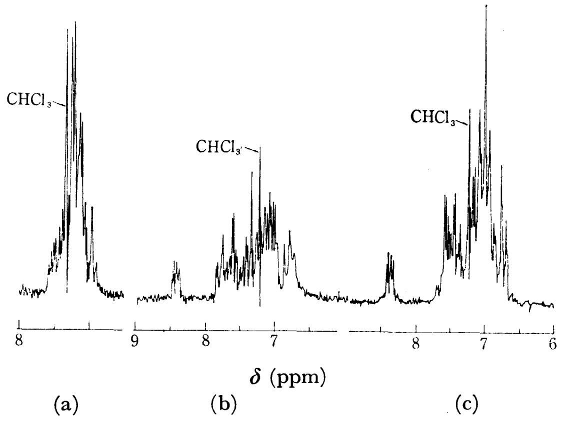


Fig. 1. NMR spectra of dimers of 2,4,5-triphenylimidazolyl in $CDCl_3$.
(a) Dimer A (IA); (b) Dimer B (IB); (c) Dimer C(IC).

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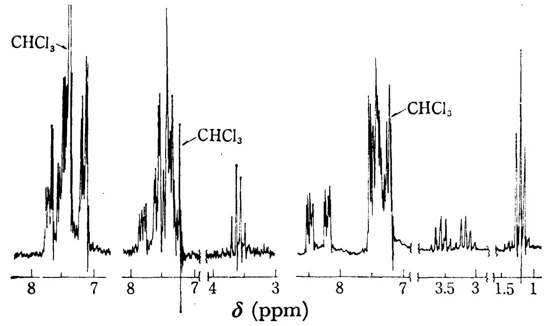
[9] D. M. White and J. Sonnenberg, *J. Amer. Chem. Soc.*, **88**, 3825 (1966).

[10] K. Maeda and T. Hayashi, This Bulletin, **42**, 3509 (1969); **43**, 429 (1970); T. Hayashi and K. Maeda, *Nippon Kagaku Zasshi*, **90**, 325 (1969).

[11] H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, **18b**, 406 (1963).

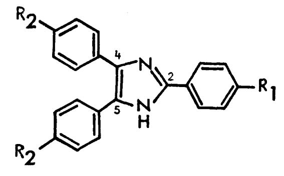
[12] Structures (b) and (c) have one asymmetric center and hence dimer B and C must be a *dl* form, whereas structure (f) has a pair of such asymmetric centers, and *d*, *l*, and meso forms are possible.

[13] A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals" Academic Press, London (1968), p. 132.



(I-N)　(I-2)　(I-4)

Fig. 2. NMR spectra of *N*-methyl-2,4,5-triphenylimidazole (I–N), 2-ethoxy-2,4,5-triphenyl-2*H*-isoimidazole (I–2) and 4-ethoxy-2,4,5-triphenyl-4*H*-isoimidazole (I–4) in CDCl$_3$.



(I) $R_1=R_2=H$
(II) $R_1=CH_3$, $R_2=H$
(III) $R_1=H$, $R_2=CH_3$
(IV) $R_1=R_2=CH_3$
(V) $R_1=Cl$, $R_2=H$
(VI) $R_1=H$, $R_2=Cl$
(VII) $R_1=R_2=Cl$
(VIII) $R_1=CH_3O$, $R_2=H$
(IX) $R_1=H$, $R_2=CH_3O$

Table 1. Properties of dimers of 2,4,5-triphenylimidazolyl and substituted 2,4,5-triphenylimidazolyls

Compd.	Substituents 2-*p*-	Substituents 4,5-di-*p*-	Recryst.[a)] solvent	Cryst. form	Mp °C (dec.)	Formula	C% Found	C% Calcd	H% Found	H% Calcd	N% Found	N% Calcd
IA	H	H	B–H	W–P	194—197[c)]	$C_{42}H_{30}N_4$	85.74	85.40	5.07	5.12	9.26	9.49
IB	H	H	B–H	Y–P	178—179	$C_{42}H_{30}N_4\cdot 1/2C_6H_6$	85.97	85.82	5.06	5.28	9.14	8.90
IC	H	H	B–H	W–P	207—209	$C_{42}H_{30}N_4$	85.64	85.40	4.83	5.12	9.19	9.49
IIA	CH_3	H	B–H	LY–P	175—176[d)]	$C_{44}H_{34}N_4$	85.31	85.41	5.24	5.54	8.96	9.05
IIB	CH_3	H	B–H	Y–Pl	178—179	$C_{44}H_{34}N_4\cdot 1/2C_6H_6$	85.74	85.81	5.79	5.67	8.78	8.52
IIC	CH_3	H	B–H	Y–P	172—173	$C_{44}H_{34}N_4$	85.64	85.41	5.66	5.54	8.92	9.05
IIIA	H	CH_3	B–H	LY–P	155—157	$C_{46}H_{38}N_4$	85.53	85.42	5.92	5.92	8.45	8.66
IIIB	H	CH_3	B–H	Y–R	145—147	$C_{46}H_{38}N_4\cdot 1/2C_6H_6$	85.92	85.81	6.27	6.03	8.29	8.17
IIIC	H	CH_3	B–H	Y–P	177—178	$C_{46}H_{38}N_4$	85.36	85.42	6.25	5.92	8.38	8.66
IVA	CH_3	CH_3	B–H	YG–P	161—162[d,e)]	$C_{48}H_{42}N_4$	85.54	85.43	6.39	6.27	8.40	8.30
IVB	CH_3	CH_3	B–H	Y–P	187—188	$C_{48}H_{42}N_4$	85.25	85.43	6.28	6.27	8.22	8.30
IVC	CH_3	CH_3	B–H	Y–P	183—185	$C_{48}H_{42}N_4$	84.99	85.43	6.41	6.27	8.03	8.30
VA	Cl	H	B–H	C–R	206—207[c,e)]	$C_{42}H_{28}N_4Cl_2\cdot 1/2C_6H_6$	77.41	77.36	4.15	4.47	8.04	8.02
VB	Cl	H	B–H	LY–P	200—202	$C_{42}H_{28}N_4Cl_2\cdot 1/2C_6H_6$	77.21	77.36	4.40	4.47	8.07	8.02
VC	Cl	H	B	W–P	179—180	$C_{42}H_{28}N_4Cl_2$	76.89	76.48	4.01	4.28	8.26	8.50
VIA	H	Cl	C–H	C–N	163—165	$C_{42}H_{26}N_4Cl_4\cdot 1/2CHCl_3$	65.34	64.76	3.64	3.39	6.95	7.11
VIB	H	Cl	B–H	Y–N	151—153	$C_{42}H_{26}N_4Cl_4\cdot 1/2C_6H_6$	70.39	70.72	4.19	3.81	7.29	7.30
VIC	H	Cl	E	LY–R	190—191	$C_{42}H_{26}N_4Cl_4$	69.40	69.25	3.42	3.60	7.77	7.69
VIIA	Cl	Cl	B–H	Y–P	207—208[c,e)]	$C_{42}H_{24}N_4Cl_6$	63.72	63.29	3.18	3.03	6.82	7.03
VIIB	Cl	Cl	B–H	Y–P	179—181	$C_{42}H_{24}N_4Cl_6$	63.82	63.29	3.03	3.03	6.87	7.03
VIIC	Cl	Cl	B–H	Y–R	~155	$C_{42}H_{24}N_4Cl_6\cdot 1/2C_6H_6$	64.53	64.62	3.36	3.25	6.81	6.70
VIIIA	OCH_3	H	B–H	Y–N	120—122	$C_{44}H_{34}N_4O_2$	81.35	81.21	5.04	5.27	8.48	8.61
VIIIB	OCH_3	H	CH	Y–P	130—131	$C_{44}H_{34}N_4O_2\cdot C_6H_{12}$	81.63	81.71	6.12	6.32	7.47	7.62
VIIIC	OCH_3	H	E	Y–P	197—199	$C_{44}H_{34}N_4O_2$	81.27	81.21	5.23	5.27	8.64	8.61
IXA	H	OCH_3	B–H	Y–N	176—177	$C_{46}H_{38}N_4O_4\cdot 1/2C_6H_6$	78.33	78.54	5.28	5.51	7.25	7.47

a) B: benzene; H: *n*-hexane; C: chloroform; E: ethanol; CH: cyclohexane.

b) W: white; Y: yellow; LY: light yellow; YG: yellow-green; C: colorless; P: powder; Pl: plates; R: rods; N: needles.

c) D. M. White and J. Sonnenberg, *J. Amer. Chem. Soc.*, **88**, 3825 (1966): IA, mp 202—202.5°C; VA, mp 203—205°C; VIIA, mp 209—210°C.

d) H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, **18b**, 406 (1963): IIA, mp 190°C; IVA, mp *ca.* 180°C; VIIIA, mp 146°C.

e) K. Maeda and T. Hayashi, This Bulletin, **43**, 429 (1970): IA: mp 199—201°C; IVA, mp 194—195°C; VA, mp 219—220°C; VIIA, mp 213—214°C.

Table 2. Characteristic NMR signals (δ in ppm; solvent $CDCl_3$)

Compound	Dimer A Signal at >8	Dimer B Signal at >8	Dimer B Broad signal	Dimer C Signal at >8	N[a] Signal at >8	2[b] Signal at >8	4[c] Singals at >8	
I	no	8.43*	6.80	8.35*	no	no	8.47*	8.18*
II (Me)	no	8.31°	6.7	8.22°				
III (Me_2)	no	8.32*	6.39	8.34*	no			
IV (Me_3)	no	8.20°	6.39	8.23°			8.36°	8.12°
V (Cl)	no	8.35°	6.7	8.26°	no		8.41°	8.19*
VI (Cl_2)	no	8.39*	6.63	8.37*	no		8.45*	8.13°
VII (Cl_3)	no	8.34°	6.72	8.22°	no		8.38°	8.10°
VIII (OMe)	no	8.39°	6.80	8.39°	no	no	8.44°	8.21*

* Signals corresponding to A_2 part of A_2X_2Y pattern.
° Signals corresponding to A_2 part of A_2X_2 pattern.
a) *N*-Methyltriarylimidazole
b) 2-Ethoxy-2,4,5-triaryl-2*H*-isoimidazole
c) 4-Ethoxy-2,4,5-triaryl-4*H*-isoimidazole

Table 3. Characteristic IR bands and R_f values

Compound	Dimer A IR[a]	Dimer A R_f[b]	Dimer B IR	Dimer B R_f	Dimer C IR	Dimer C R_f	N[c] IR	2[d] IR	4[e] IR
I	1604 m	0.25	1610 s	0.33	1613 vs	0.40	1605 m	1607 w	1612 vs
II (Me)	1602 m	0.21	1608 vs	0.30	1613 vs	0.35			
III (Me_2)	1610 m	0.22	1609 vs	0.29	1616 vs	0.38			
IV (Me_3)	1613 m	0.21	1605 vs	0.30	1618 vs	0.39			
V (Cl)	1605 m	0.35	1609 vs	0.38	1619 vs	0.42	1603 m		1610 vs
VI (Cl_2)	1600 m	0.36	1608 s	0.39	1621 vs	0.49	1605 vw		1613 vs
VII (Cl_3)	1600 m	0.38	1605 s	0.43	1620 s	0.47	1600 vw		1612 vs
VIII (OMe)	1609 m	0.09	1604 s	0.15	1611 s	0.23	1611 m	1609 m	1611 vs

a) ν (KBr) cm^{-1}; w: weak, m: medium, s: strong, v:very.
b) R_f value on silica gel tlc (Merck Kieselgel $PF_{254+366}$; benzene:ethyl acetate=20:1)
c) *N*-Methyltriarylimidazole
d) 2-Ethoxy-2,4,5-triaryl-2*H*-isoimidazole
e) 4-Ethoxy-2,4,5-triaryl-4*H*-isoimidazole

other three dimers, A, B, and C, could give their NMR spectra, but these spectra were too complicated to be analyzed (Fig. 1). Therefore, we have synthesized lophines (II–IX) having mono-, di-, and tri-*p*-substituents on the phenyl groups; each compound in turn has been oxidized to the three dimers corresponding to the lophyl dimers, A, B, and C, as shown in the Table 1. The structural correlation of these dimers to the parent lophyl dimers has been carried out by careful comparisons of the chemical shifts and coupling patterns of their NMR spectra, characteristic IR bands between 1400 and 1700 cm^{-1}, R_f values on tlc, and photochromic property. Some of the characteristic properties of the three series of dimers are as follows. Dimer A series gives no NMR signal at a lower field than 8 ppm, whereas a two-proton signal appears around 8.3 ppm in the NMR spectra of dimer B and C series. Furthermore, NMR spectra of dimer B series show a characteristically broad signal around 6.5 ppm. Dimer B and C series give a very strong IR band around 1600 cm^{-1}; a compound which belongs to the latter series always gives a bond at a higher frequency than that of the corresponding compound in the former series. Dimer A series of compounds also gives IR band around 1600 cm^{-1}, but intensity of this band is distinctly lower than those of other series. The data are summerized in Tables 2 and 3. The *p*-substituted phenyl groups gave A_2X_2 or A_2B_2 type NMR signals which could be analyzed fairly easily, and at the same time, the signals of the substituents such as CH_3 and OCH_3 could also be used for the structural elucidation. Selection of suitable compounds and suitable NMR conditions (temperature, solvents, *etc.*) made analysis of the signals possible. The results are as follows:

(1) Since the NMR spectrum of dimer B of 2,4,5-tri(*p*-tolyl)imidazolyl (IVB) shows well separated six A_2X_2 patterns of the tolyl grops (Fig. 3b;[14] all of the ortho coupling constants are 8.5 Hz) and six methyl singlets (solvent, $CDCl_3$; δ 1.98, 2.14, 2.17, 2.22, 2.35, and 2.48 ppm), dimer B has six magnetically different phenyl groups and hence the structure (b)[12] must be assigned for the dimer B.

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[14] The NMR spectrum of dimer B of tri(*p*-tolyl)imidazolyl (IVB) at room temperature shows a broad signal at 6.39 (in $CDCl_3$) ppm, which is spin coupled with the doublet at 7.48 ppm. This broad signal becomes a doublet by elevation of the measuring temperature to 60°C. This phenomenon would be attributable to the restricted rotation of a phenyl group about the C–C bond between the phenyl and the imidazole ring. This characteristic broad band can be used for identification of a series of dimer B (Table 2). Further discussion on this phenomenon will be reported elsewhere.

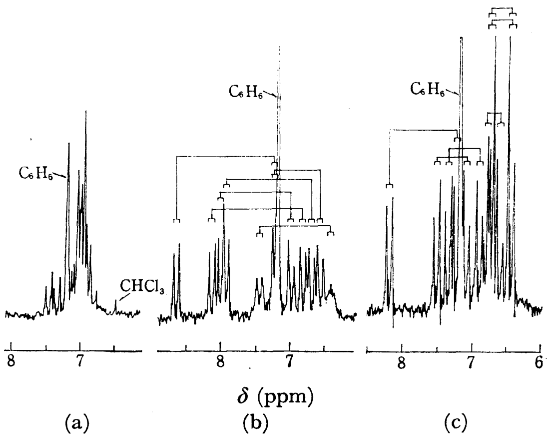

Fig. 3. NMR spectra of dimers of 2,4,5-triarylimidazolyl.
(a) Dimer A of 2.4,5-tri(*p*-chlorophenyl)imidazolyl (VIIA) in $C_6D_6+CDCl_3$ (3:2).
(b) Dimer B of 2,4,5-tri(*p*-tolyl)imidazolyl (IVB) in C_6D_6; the spin couplings indicated were confirmed by spin decoupling experiments.
(c) Dimer C of 2,4,5-tri(*p*-chlorophenyl)imidazolyl (VIIC) in C_6D_6; the spin couplings indicated (except one) were confirmed by spin decoupling experiments.

(2) The NMR spectrum of dimer C of 2,4,5-tri(*p*-chlorophenyl)imidazolyl (VIIC) in benzene-d_6 (Fig. 3c) shows in addition to well separated four A_2X_2 (or A_2B_2) patterns, each of which corresponds to four protons, an A_2B_2 pattern corresponding to eight protons, which indicates the presence of a pair of magnetically equivalent *p*-chlorophenyl groups (all of the ortho coupling constants are 8.5 Hz). This was further confirmed by analysis of the methyl signals of tri(*p*-tolyl)imidazolyl dimer C (IVC) (Fig. 4); there always exists a singlet signal corresponding to two methyl groups. Hence, the possible structures for dimer C are restricted to (a) or (c).[15]

(3) Dimer B and C have a low-field signal (δ *ca.* 8.4 ppm in $CDCl_3$) (Fig. 1 and Table 2), which is attributable to two ortho-protons of one of the two 2-phenyl groups, since the low-field signal becomes A_2X_2 pattern by introduction of a *p*-substituent on the 2-phenyl group of the dimer B and C (Table 2). Such a low-field signal exists in the NMR spectrum of 3-ethoxy-2,4,5-triphenyl-4*H*-isoimidazole (I-4), but not in those of 2-ethoxy-2,4,5-triphenyl-2*H*-isoimidazole (I-2) and *N*-methyl-2,4,5-triphenylimidazole (I-N) (Fig. 2), indicating that the signal is due to the 2-phenyl group of 4*H*-isoimidazole ring. Incidentally, the signal at δ 8.18 ppm in the NMR spectrum of the 4-ethoxy derivative (I-4) corresponds to the ortho protons in the 4-phenyl group, since (V-4) and (VI-4) gave in this region a signal having A_2 part of A_2X_2Y and A_2X_2 patterns, respectively; the low-field shift of this signal being attributable to the attachment of oxygen atom at 4-position. Dimer B and C, therefore, have a 2,4,5-triphenyl-4*H*-isoimidazolyl group linked at C_4; thus, possible structures being (b), (c), and (f). Since the structure of dimer C is already restricted to (a) or (c), above results indicate that the structure of dimer C must be represented by (c).[12]

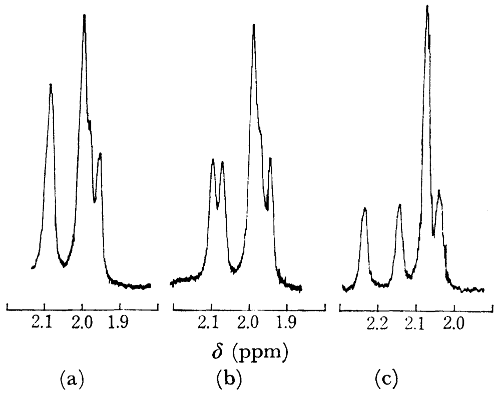

Fig. 4. Methyl signals in the NMR spectra of dimer C of 2,4,5-tri-(*p*-toyl)imidazolyl (IVC).
(a) in C_6D_6; (b) in $C_6D_6+CDCl_3$ (4:1); (c) in $C_6D_6+CDCl_3$ (4:5).

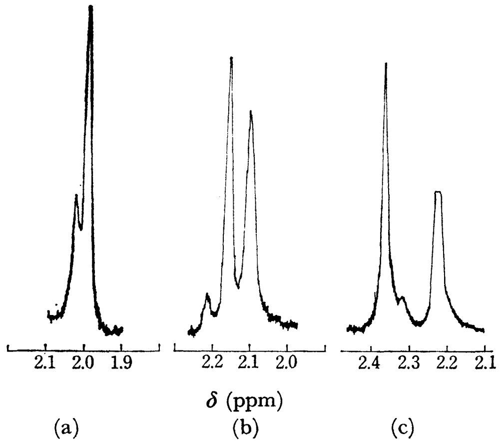

Fig. 5. Methyl signals in the NMR spectra of dimer A of 2-phenyl-4,5-di(*p*-tolyl)imidazolyl (IIIA). (a) in C_6D_6; (b) in $C_6D_6+CDCl_3$ (1:1); (c) in $CDCl_3$.

(4) The NMR signals of dimer A (Fig. 1a) appears in a narrow range (6.8—7.7 ppm in $CDCl_3$) and not well resolved, but analysis of the methyl signals of dimer A of 4,5-di(*p*-tolyl)-2-phenylimidazolyl (IIIA) indicates that two of the four methyl groups are in a magnetically identical environment (Fig. 5), whereas each of other two methyl groups is in a different environment from others. Since 4*H*-isoimidazolyl moiety is not involved in this dimer, structure (a) must be assigned to dimer A. This assignment is also supported by the NMR spectrum of the dimer A of 2,4,5-tri(*p*-chlorophenyl)imidazolyl (Fig. 3a), which indicates that at least the symmetrical structures, (d), (e), and (f), can be excluded (two-proton doublets at 7.34 and 7.46 ppm).

Infrared spectra also support these assignments (Fig. 6 and Table 3). The 4-ethoxy compound (I-4) has a very strong IR band at 1612 cm^{-1}, whereas 2-ethoxy (I-2) and *N*-methyl (I-N) compounds have only a medium but sharp band around 1600 cm^{-1}; thus, the strong band at 1612 cm^{-1} indicates the presence of 4*H*-isoimidazole ring. Dimer B and C, which have a

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[15] Structure (c) has an asymmetric carbon atom, and hence two phenyl groups at the 4 and 5 positions of 2*H*-isoimidazolyl group is in principle magnetically non-equivalent, but magnetic influence of the asymmetric center would be negligibly small, since it is far apart from the phenyl groups.

Table 4. Properties of *N*-methyl-2,4,5-triarylimidazoles, and 2-ethoxy- and 4-ethoxy-2,4,5-triarylisoimidazoles

Compd.	Substituents		Recryst.[a] solvent	Cryst.[b] form	Mp °C	Formula	C%		H%		N%	
	2-*p*-	4,5-di-*p*-					Found	Calcd	Found	Calcd	Found	Calcd
I-N	H	H	CH	C–N	143[c]	$C_{22}H_{18}N_2$	85.35	85.13	5.93	5.85	9.17	9.09
I-2	H	H	E	C–R	138	$C_{23}H_{20}N_2O$	81.03	81.15	5.83	5.92	8.23	8.23
V-N	Cl	H	EA	C–N	194	$C_{22}H_{17}N_2Cl$	76.15	76.62	4.82	4.98	8.07	8.13
V-4	Cl	H	E	C–P	130—131	$C_{23}H_{19}N_2OCl$	73.52	73.97	4.96	5.12	7.47	7.47
VI-N	H	Cl	E	Y–N	188—189	$C_{22}H_{16}N_2Cl_2$	69.75	69.66	4.25	4.26	7.48	7.39
VI-4	H	Cl	E	C–P	130	$C_{23}H_{18}N_2OCl_2$	67.46	67.97	4.53	4.44	6.71	6.85
VII-N	Cl	Cl	E	Y–Pl	204—205	$C_{22}H_{15}N_2Cl_3$	63.70	63.86	3.56	3.66	6.81	6.77
VII-4	Cl	Cl	E	C–N	148—149	$C_{23}H_{17}ON_2Cl_3$	62.06	62.25	3.61	3.86	6.44	6.31
VIII-N	OCH_3	H	EA	C–N	174—175	$C_{23}H_{20}N_2O$	81.38	81.15	5.68	5.92	8.28	8.23
VIII-2	OCH_3	H	E	C–Pl	134—136	$C_{24}H_{22}N_2O_2$	78.15	78.81	6.06	5.99	7.60	7.56
VIII-4	OCH_3	H	E	C–P	145—146	$C_{24}H_{22}N_2O_2$	77.86	77.81	6.07	5.99	7.56	7.56

a) and b): see footnotes of Table 1; EA: ethyl acetate.
c) D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964): I-N: mp 143.5—144.5°C.

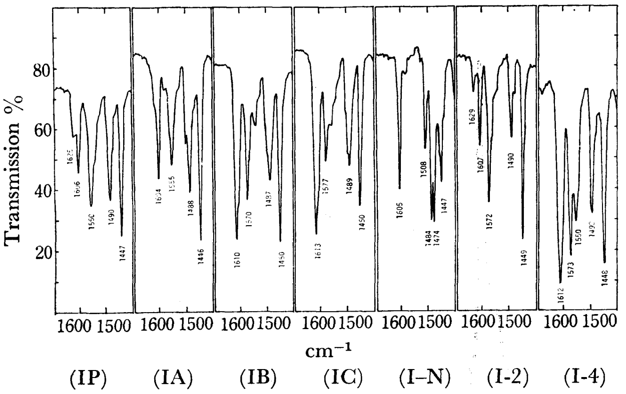
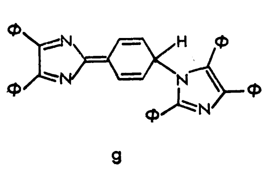
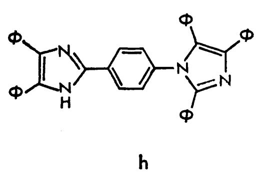


Fig. 6. IR spectra between 1400 and 1700 cm^{-1} in KBr disc. IP: piezochromic dimer of I; IA: dimer A of I; IB: dimer B of I; IC: dimer C of I; I-N: *N*-methyltriphenylimidazole; I-2: 2-ethoxytriphenylisoimidazole; I-4: 4-ethoxytriphenylisoimidazole.

4*H*-isoimidazole ring, indeed show a strong band at *ca.* 1610 cm^{-1}. On the other hand, a sharp medium band is present at 1604 cm^{-1} in the IR spectrum of dimer A indicating the absence of 4*H*-isoimidazole ring and the presence of 2*H*-iso- and/or imidazole ring.[16)]



g

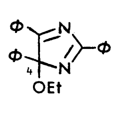


h

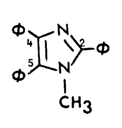
Since these three dimers can be prepared without difficulty from tri-*p*-substituted lophines, the structures involving the linkage at the *p*-position of one of the phenyl groups such as structure (g) are excluded.[17)] Furthermore, since they show no NH band in their IR spectra as indicated by White and Sonnenberg[9)] and since they can be interconverted thermally, the structures such as (h), in which a triphenylimidazole is substituted at a *p*-position of a phenyl group of another triphenylimidazole, are excluded.

It is of interest to note that the photochromic dimers, A and B, have the central C–N bond, whereas non-photochromic dimer C has the central C–C bond. In the former case the excitation energy is transferred from the aromatic imidazole ring to the central C–N bond, which is directly attached to the aromatic ring, whereas in the latter case, it is not, since the central C–C bond is separated by an *sp*^{3} carbon atom from the conjugated systems.

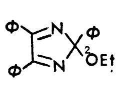
2-Ethoxy-2*H*- (I-2) and 4-ethoxy-4*H*-2,4,5-triphenylisoimidazole (I-4) were prepared from lophyl dimer A (IA) by dissolving in ethanol and treating with dilute hydrochloric acid; the central C–N bond of this dimer being cleaved heterolytically. The 4-ethoxy compound



(I-4)



(I-N)



(I-2)

(I-4) has an asymmeric carbon atom and hence its NMR spectrum (Fig. 2) shows non-equivalence of the methylene protons in the ethoxy group, whereas only a quartet signal was observed for the methylene protons in the case of 2-ethoxy compound (I-2). Derivatives of these ethoxy compounds are listed in Table 4. The 4-ethoxy compound (VIII-4) seems to be more stable

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16) The piezochromic dimer is rapidly converted to dimer A by dissolving it in organic solvents such as benzene, ethyl acetate, chloroform, acetone, and ether and followed by immediate evaporation at room temperature. Hence, its NMR, UV, and IR spectra in solutions could not be obtained. IR spectrum taken in KBr disc is only the available physical data for structural analysis. Although White and Sonnenberg[9)] suggested the structure (f) for the piezochromic dimer by analysis of its IR spectrum; the piezochromic dimer shows only a medium band at 1606 cm^{-1} with a shoulder at 1625 cm^{-1}, and hence the structure (e) (or less probably (d)) would be more probable than (f). The piezochromic dimers obtained from other lophine derivatives may be impure compounds contaminated with the starting lophine derivative and the corresponding dimer A.

17) The structure of dimer of triphenylmethyl has recently been revised from the symmetric hexaphenylethane to the asymmetric structure similar to (g). H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, **1968**, 249; H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, **103**, 1101 (1970).

than 2-ethoxy compound (VIII-2), since the latter isomerizes to the former by treatment with acid.

N-Methyllophine (I-N) was prepared by treatment with dimethyl sulfate and potassium carbonate in boiling acetone. Synthesized derivatives of the *N*-methyl compound are listed in Table 4.

Experimental

All melting points are uncorrected. IR spectra were recorded on a JASCO IR-G grating spectrophotometer and NMR spectra on a JEOL 4H-100 (100 MHz) spectrometer. Chemical shifts are expressed in ppm from internal tetramethylsilane (δ-value) and coupling constants in Hz.

Lophine (I) and Substituted Lophines (II-IX). These compounds were synthesized by the method of Davidson *et al.*[18] by refluxing the appropriate benzil with the appropriate aldehyde and ammonium acetate in acetic acid for *ca.* 1 hr. The reaction mixture was then poured into ice-water and the precipitated product was collected. (Solvent in parentheses was used for crystallization) Lophine (I), colorless needles (methanol), mp 275—276°C, lit, 274—275°C.[19] 2-*p*-Tolyl-4,5-diphenylimidazole (II), needles (methanol), mp 233—237°C, lit, mp 234—235°C.[19] 2-Phenyl-4,5-di(*p*-tolyl)imidazole (III), needles (ethanol), mp 269—271°C. Found: C, 85.31; H, 6.18; N, 8.62%. Calcd for $C_{23}H_{20}N_2$: C, 85.15; H, 6.21; N, 8.64%. 2,4,5-Tri(*p*-tolyl)imidazole (IV), pale yellow needles (methanol), mp 237—240°C, lit,[20] 234°C. 2-*p*-Chlorophenyl-4,5-diphenylimidazole (V), colorless needles (ethanol), mp 264—265.5°C, lit, 284—286°C.[19] (Found: C, 76.54; H, 4.24; N, 8.46%). 2-Phenyl-4,5-di(*p*-chlorophenyl)imidazole (VI), colorless needles (ethyl acetate), mp 294—295°C. Found: C, 68.48; H, 3.61; N, 7.74%. Calcd for $C_{21}H_{14}N_2Cl_2$: C, 69.06; H, 3.86; N, 7.67%. 2,4,5-Tri(*p*-chlorophenyl)imidazole (VII), pale yellow needles (ethyl acetate), mp 276—278°C, lit, 275—275.5°C.[21] 2-*p*-Anisyl-4,5-diphenylimidazole (VIII), colorless needles (ethanol), mp 232—233°C, lit, 233—233.5°C.[4] 2-Phenyl-4,5-di(*p*-anisyl)imidazole (IX), pale yellow plates (ethanol), mp 99—100°C, lit, 197°C,[4] 99°C.[22] Found: C, 70.40; H, 6.26; N, 6.62%. Calcd for $C_{23}H_{20}N_2O_2 \cdot 2H_2O$: C, 70.39; H, 6.16; N, 7.14%.

Piezochromic Dimers of Lophine and Substituted Lophines. According to the method of White and Sonnenberg,[9] to a solution of lophine (2 g) in 95% ethanol (200 m*l*) containing potassium hydroxide (24 g) was added under ice cooling at 5—10°C with stirring 1% aqueous potassium ferricyanide (900 m*l*) in a period of 3 hr and the mixture was stirred for additional 1 hr. The precipitated solid was collected on a filter, washed with water and dried over phosphorus pentoxide to give piezochromic dimer as pale violet powder, mp *ca.* 141°C (yield 95%), lit, 187.5—188.5°C,[9] 191—192°C.[10] Piezochromic dimers from substituted lophines (II—IX) were also prepared in a similar way, but IR spectra indicated that they may be impure and contaminated with the corresponding dimer A and starting material. Melting points (decomp.) are as follows: piezochromic dimer from II, mp 109—112°C; from III, 128—132°C; from IV, mp *ca.* 122°C; from V, mp 110—124°C, lit, 195—200°C,[9] 205—207°C;[10] from VII, mp *ca.* 123°C, lit, 105—115°C;[9] from VIII, mp *ca.* 111°C; from IX, mp *ca.* 125°C.

Dimer A of Lophine and Substituted Lophines (IA—IXA). The dimers, IA, VA, VIA, VIIA, VIIIA, and IXA, were prepared by crystallization of the corresponding piezochromic dimer from benzene–*n*-hexane (Table 1). The *p*-methyl derivatives, IIA, IIIA, and IVA, could not be obtained in a pure state from the corresponding piezochromic dimer by crystallizations, and hence they were prepared from the corresponding dimer B in the following way. A solution of IIB (200 mg) in benzene (15 m*l*) was irradiated with a fluorescent lamp (National High-light, 15 W) at room temperature for 13 hr and then evaporated to dryness *in vacuo.* Dimer A was separated from the remaining solid by means of silica gel tlc as a dark brown amorphous solid, which was crystallized from benzene–*n*-hexane yielding IIA (136 mg) as a crystalline powder. IIB (7 mg) was also recovered.

Dimers B and C of Lophine and Substituted Lophines. A solution of piezochromic dimer of lophine (300 mg) in benzene (15 m*l*) was refluxed for 20 hr and then evaporated to dryness *in vacuo* to give a yellow amorphous solid. The solid was subjected to silica gel tlc (Kieselgel $PF_{254+366}$; benzene: ethyl acetate=20: 1) in the dark to afford three dimers, A, B, and C, each of which was purified by crystallization from a suitable solvent. The fraction of dimer A was usually contaminated with the monomer and this method was not suitable for preparation of dimer A. Dimers B and C of substituted lophines (II—VIII) were prepared in a similar way from the appropriate piezochromic dimer (Table 1).

Preparation of Three Dimers, A, B, and C, by Oxidation with Lead Dioxide. A mixture of lophine (2 g) and lead dioxide (8 g), which was freshly prepared from lead tetraacetate by treatment with water, in benzene (150 m*l*) was refluxed with stirring for 20 hr and filtered while in hot through Hyflo-supercel. The filtrate on evaporation to a small volume precipitated white crystals (195 mg, lophine), which were filtered off. The filtrate was evaporated to dryness *in vacuo* and the residue was subjected to tlc as described above to give three components, which were identical with the dimers, A, B, and C. Yields (crude) were 475 mg (dimer A), 340 mg (dimer B), and 809 mg (dimer C). Lophine (195 mg) was also recovered.

*2-Ethoxy-2,4,5-triphenyl-2*H*-isoimidazole (I-2) and 4-Ethoxy-2,4,5-triphenyl-4*H*-isoimidazole (I-4) and Their Derivatives.* A solution of the dimer IA (1 g) in dichloromethane (80 m*l*) and ethanol (160 m*l*) was treated with a drop of concentrated hydrochloric acid and the mixture was refluxed for 3 hr. After neutralization with dil. aqueous sodium hydrogen carbonate, the reaction mixture was evaporated to dryness *in vacuo* and the residue was extracted with chloroform. The chloroform extract was evaporated and the residue was subjected to tlc on silica gel (benzene: ethyl acetate=20: 1) to give 4-ethoxy compound (I-4) (112 mg), 2-ethoxy compound (I-2) (115 mg), lophine (I) (276 mg) and recovered IA (271 mg) (Table 4). 4-Ethoxy compound (I-4) could not be crystallized but mass (*m/e* 340), NMR (Fig. 2), and IR (Fig. 6) spectra indicate its identity. Other 2-ethoxy and 4-ethoxy compounds of substituted lophines listed in Table 4 were prepared in a similar way from the appropriate dimer A.

*Conversion of 2-Ethoxy-2-anisyl-4,5-diphenyl-2*H*-isoimidazole (VIII-2) to 4-Ethoxy-2-anisyl-4,5-diphenyl-4*H*-isoimidazole (VIII-4).* A solution of VIII-2 (30 mg) in ethanol (3 m*l*) was treated with a drop of hydrochloric acid in ethanol (concentrated HCl: ethanol=1:9) and the mixture was allowed to stand at room temperature for 3 days. After neutraliza-

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[18] D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1957).

[19] G. E. Philbrook, M. A. Maxwell, R. E. Taylor, and J. R. Totter, *Photochem. Photobiol.*, **4**, 1175 (1965).

[20] L. Gattermann, *Ann. Chem.*, **347**, 367 (1906).

[21] D. M. White and J. Sonnenberg, *J. Org. Chem.*, **29**, 1926 (1964).

[22] Gevaert, Photo-Producten, N. V., *Chem. Abstr.*, **58**, 2530 (1963).

tion with aqueous sodium hydrogencarbonate, the mixture was evaporated to dryness *in vacuo* and the residue was subjected to silica gel tlc (benzene: ethyl acetate=20: 1) to give 4-ethoxy compound (VIII-4) (16 mg) and 2-ethoxy compound (VIII-2) (4 mg). The similar treatment of 4-ethoxy compound (VIII-4) gave no 2-ethoxy compound (VIII-2).

N-*Methyl-2,4,5-triphenylimidazole and Its Derivatives.* To a solution of lophine (1 g) and dimethyl sulfate (640 mg) in acetone (45 m*l*) was added powdered anhydrous potassium carbonate (700 mg) and the mixture was refluxed with stirring for 5 hr. After cooling, the mixture was poured into water (150 m*l*) and the precipitated white crystals were collected by filtration and recrystallized from *n*-hexane to give colorless needles (522 mg), mp 143°C.[21] Other *N*-methyl derivatives listed in Table 4 were prepared in a similar way; yields being about 50%.

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