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OXIDATIVE DIMERIZATION OF PYRROLE DERIVATIVES

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Several N-hetero aromatic compounds have been known to form dimers via oxidation and some of these to be in equilibrium with dissociated radicals.[1a-g] However the structure of the dimers, which are often depicted as hydrazine derivatives (N-N bond), are in doubt and require further confirmation.[2] In the pyrrole series, tetraphenylpyrrole was the only case, but the structure of the dimer has not been investigated.[1acdef] In this communication, we would like to report the first structural elucidation of pyrryl radical dimers obtained from 4,5-diaryl-3-acyl-substituted pyrrole derivatives.

As an example, to an ethanolic solution of 2-methyl-3-acetyl-4,5-(bis-p-methoxyphenyl)-pyrrole[3], Ia, an aqueous potassium ferricyanide and potassium hydroxide was added with stirring at room temperature. A crystalline precipitate of IIa was formed quantitatively, and recrystallized from ethanol, benzene-petroleum ether or acetone to give an analytically and spectrometrically pure sample, mp 150-155° (decomp.). This showed following properties. M. w. 595.4 (osmometric method, 37° in $CHCl_3$). Mass spectrum, m/e 668 (M^+). Anal. $C_{42}H_{40}O_6N_2$.

Elemental analysis and molecular weight data support the formation of pyrryl radical dimer, IIa. The dimer still contains the pyrrole ring, since the reduction of IIa with hydroquinone in benzene affords Ia quantitatively. The single $C\underline{H}_3$ signal at 1.40 ppm and $COC\underline{H}_3$ at 2.20 ppm in NMR spectra suggested a symmetrical dimer structure. Two overlapping A_2B_2 type signals in the aromatic region indicated that the phenyl rings were not involved in the dimerization bond formation.[4]

Furthermore, the $2\text{-}C\underline{H}_3$ in Ia at 2.60 ppm shifted to 1.40 ppm in IIa.

This only allows for IIa a structure in which the carbons at the 2, 2' position are connected to each other,[5] as shown in Scheme I. In addition, strong imine absorptions at 1610 cm^{-1} and those of an α, β-unstd. ketone at 1695 cm^{-1} in IR spectra also support the pyrrolenine structure for IIa. Analogous reaction of some other derivatives, Ib-f, gave the corresponding dimers, IIb-f, shown in Table I. Their UV spectra (illustrated in Fig. 1) showed that para-substituents on the phenyl ring at 4(4') position had little effect on the absorption pattern in comparison with those at 5(5'). Therefore, in those dimers, the 4-phenyl substituents are almost certainly bent out of plane by a steric effect to a greater degree than the 5-phenyl substituents, since the latter are adjacent to the unsubstituted nitrogen atom. This would support the steric structure illustrated in Fig. 2. Of course, since these dimers contain two asymmetric carbons at 2, 2', both dl and meso isomers are possible, but a meso form might be favoured owing to a steric effect.

In the usual organic solvents, IIa, -b, -c and -e showed weak thermochromism; at temperatures above 60°, the colorless solution became light red (λmax. 555 mμ) and the red color disappeared at room temperature reversibly. As expected, temperature dependent reversible radical dissociation of the dimers was verified by ESR technique. The interpretation of hyperfine structure patterns in the ESR spectra, which will be given in the forthcoming paper, also support the position at which dimerization takes place. In the case of IIf, obvious coloration was not observed under the same conditions. It was not inconsistent with the results obtained by Zimmerman and his co-workers[1g] who have shown that para-electron donating substituents (especially the methoxy group) are the most effective in radical dissociation. The reason why IId also does not show thermochromism is explainable from the lack of this p-methoxy substituent effect since the phenyl substituent containing the methoxy group in this compound is bent out of plane, as shown above.

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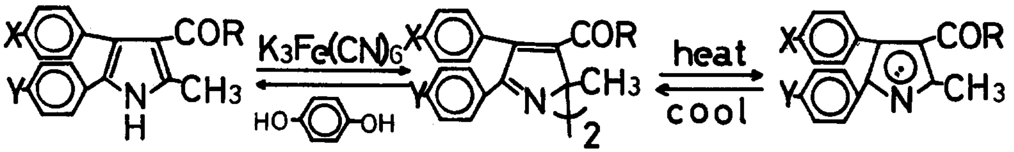
Scheme I



Ia-f IIa-f IIIa, b, c, e

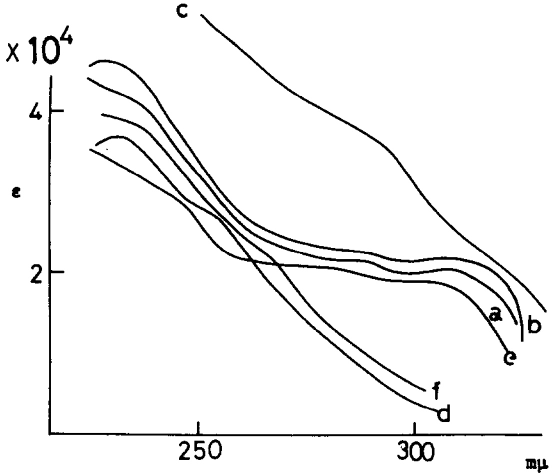
	X	Y	R		X	Y	R
a;	X=OCH$_3$	Y=OCH$_3$	R=CH$_3$	d;	X=OCH$_3$	Y=H	R=CH$_3$
b;	OCH$_3$	OCH$_3$	C$_2$H$_5$	e;	H	OCH$_3$	CH$_3$
c;	OCH$_3$	OCH$_3$	C$_6$H$_5$	f;	H	H	CH$_3$

Table I

	mp °C	IR(CO) cm^{-1}	NMR(2-CH$_3$) ppm(CDCl$_3$)		mp(decomp.) °C	IR(CO, C=N) cm^{-1}		NMR(CH$_3$) ppm(CDCl$_3$)	M. W. 37°C, CHCl$_3$	Mass m/e(M$^+$)
Ia	193.5-195.5	1630	2.60	IIa	150-155	1695	1610	1.40	595.4	668
b	155-158	1640	2.60	b	140-145	1695	1610	1.40	706.6	696
c	237-239	1625	2.40	c	185-190	1645	1600	*	*	792
d	195-198.5	1640	2.60	d	130-155	1695	1610	1.45	638.3	608
e	204-207	1640	2.60	e	150-155	1695	1610	1.45	596.0	608
f	167-170	1640	2.60	f	130-142	1690	1625	1.50	518.8	548

* not soluble in the usual solvents

Fig. I



UV spectra of IIa-f(EtOH)

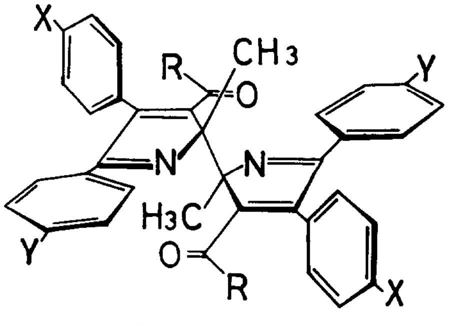


Fig. 2

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Very recently, T. Goto et al. proposed asymmetric structures for some dimers of 2,4,5-tri-aryl substituted imidazole derivatives. NMR Symposium, at Kanazawa, Japan, (Oct. 1970).

3 The synthetic methods of comp. Ia-f will be published in near future.

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