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Synthesis and Properties of 5-Substituted 2-Thiobarbituric Acid Dyes*

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SUMMARY

*The systematic synthesis of 5-substituted 2-thiobarbituric acid dyes (5-*p*-methoxy- and 5-*p*-dimethylamino-benzylidene-, cinnamylidene-, and phenylpentadienylidene-1,3-disubstituted 2-thiobarbituric acids) is described and their absorption characteristics are reported.*

1 INTRODUCTION

The spectrophotometric determination of Ag(I) with 5-*p*-dimethylaminobenzylidene-2-thiobarbituric acid (**3n**) has been previously studied and two simple and rapid methods proposed.[2] 5-*p*-Dimethylaminocinnamylidene-1-phenyl-2-thiobarbituric acid (**3t**) has also been shown to be useful for the determination of trace amounts of Au(III) with a high sensitivity.[3] Furthermore, we have reported that *p*-dimethylaminophenylpentadienal (**1f**), prepared by the new method, is a convenient reagent for the colorimetric determination of primary aromatic amines using the formation of the Schiff bases and then protonating in trichloroacetic acid medium.[4] Recently, 1,3-diphenyl-2-thiobarbituric acid has been shown to be useful for the determination of lipoperoxides in biological fluids, giving rise to pigments.[5]

In this present paper, the synthesis of two series of 5-substituted 2-thiobarbituric acid dye (**3**) is described, together with an examination of their

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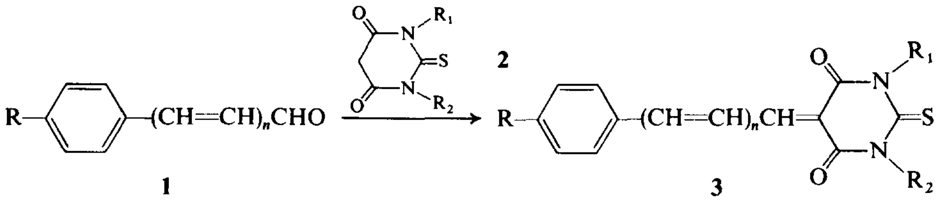
spectral properties with the aim of utilizing the compounds as analytical reagents for some heavy metal ions.

2 RESULTS AND DISCUSSION

The synthesis of **3** was carried out by the condensation of *p*-substituted benzaldehydes (**1a**–**1f**) with 1,3-disubstituted-2-thiobarbituric acids (**2**) as outlined in Scheme 1. All these products were crystalline, coloured, and stable to light, air and prolonged heating. Melting points and analytical data of **3** are listed in Table 1. In general, the compounds **3** have relatively high melting points, with the exception of **3d** and **3e**.

The visible absorption spectral data in dimethyl sulfoxide (DMSO) are shown in Table 2. Throughout the series, the colour of the compounds becomes progressively deeper as the length of the ethylenic chain is increased. As shown in Table 2, the range of the red shifts of the series in DMSO is clearly demonstrated by the large red shifts (Δ nm) shown. In particular, the bathochromic shift resultant from introduction of a dimethylamino group into the substituted benzene ring is larger than from methoxy substitution. Almost no influence of the various *N*,*N*′-substituents on the thiobarbituric acid ring is observed. However, it is noted that the substituent effects were apparent in both the series **3r**–**3u** and **3v**–**3y**, and **3y** showed the largest red shift. The reason for this is not clear at present.

All these dyes have large molar absorptivities and are therefore advantageous for use as highly sensitive colorimetric reagents. However, their solubility is very poor in most solvents and we are now studying modifications in the dyes to produce more readily soluble dyes, thus making



1	*R*	*n*
1a	OMe	0
1b	OMe	1
1c	OMe	2
1d	NMe_2	0
1e	NMe_2	1
1f	NMe_2	2

Scheme 1

TABLE 1
5-Substituted 2-Thiobarbituric Acids **3**

Compound	*M.p.* (°*C*)	*Molecular formula*	*Elemental analysis* (%) *Calc.* (*Found*)			
			C	*H*	*N*	*S*
3a	222–224	$C_{12}H_{10}N_2O_3S$	55·0	3·8	10·7	12·2
			(54·7)	(3·8)	(10·4)	(12·2)
3b	250–252	$C_{13}H_{12}N_2O_3S$	56·5	4·4	10·1	11·6
			(56·3)	(4·3)	(10·3)	(11·7)
3c	277	$C_{18}H_{14}N_2O_3S$	63·9	4·2	8·3	9·5
			(63·6)	(4·2)	(8·1)	(9·5)
3d	173–174	$C_{14}H_{14}N_2O_3S$	57·9	4·9	9·7	11·0
			(57·9)	(4·8)	(9·5)	(11·1)
3e	180–182	$C_{24}H_{18}N_2O_3S$	69·6	4·4	6·8	7·7
			(69·4)	(4·3)	(6·5)	(7·5)
3f	>300	$C_{14}H_{12}N_2O_3S$	58·3	4·2	9·7	11·1
			(58·0)	(4·1)	(5·6)	(10·9)
3g	228–231	$C_{15}H_{14}N_2O_3S$	59·6	4·7	9·3	10·6
			(59·5)	(4·6)	(9.3)	(10·5)
3h	268–270	$C_{20}H_{16}N_2O_3S$	65·9	4·4	7·7	8·8
			(65·9)	(4·5)	(7·4)	(8·8)
3i	221–224	$C_{16}H_{16}N_2O_3S$	60·7	5·1	8·9	10·1
			(60·2)	(5·1)	(8·8)	(10·2)
3j	232–235	$C_{16}H_{14}N_2O_3S$	61·1	4·5	8·9	10·2
			(60·9)	(4·4)	(8·7)	(10·2)
3k	250	$C_{17}H_{16}N_2O_3S$	62·2	4·9	8·5	9·8
			(62·4)	(4·8)	(8·4)	(9·8)
3l	236–237	$C_{22}H_{18}N_2O_3S$	67·7	4·7	7·2	8·2
			(67·9)	(4·6)	(7·1)	(8·1)
3m	249	$C_{18}H_{18}N_2O_3S$	63·1	5·3	8·2	9·4
			(63·3)	(5·2)	(8·2)	(9·3)
3n	269–270	$C_{13}H_{13}N_3O_2S$	56·7	4·8	15·3	11·6
			(56·7)	(4·7)	(15·2)	(11.6)
3o	260–261	$C_{14}H_{15}N_3O_2S$	58·1	5·2	14·5	11·1
			(58·1)	(5·2)	(14·4)	(10·9)
3p	266–267	$C_{19}H_{17}N_3O_2S$	65·0	4·9	12·0	9·1
			(64·5)	(4·8)	(11·7)	(9·0)
3q	254–255	$C_{15}H_{17}N_3O_2S$	59·4	5·7	13·9	10·6
			(59·5)	(5·6)	(13·9)	(10·4)
3r	264–265	$C_{21}H_{19}N_3O_2S$	59·8	5·0	14·0	10·6
			(59·9)	(5·0)	(14·1)	(10·7)
3s	259–260	$C_{16}H_{17}N_3O_2S$	60·9	5·4	13·3	10·2
			(60·9)	(5·4)	(13·3)	(10·2)
3t	257	$C_{21}H_{19}N_3O_2S$	66·8	5·1	11·1	8·5
			(66·9)	(5·2)	(11·1)	(8·5)
3u	248–249	$C_{17}H_{19}N_3O_2S$	62·0	5·8	12·8	9·7
			(61·9)	(5·9)	(12·8)	(9·8)
3v	273–274	$C_{17}H_{17}N_3O_2S\cdot$	60·7	5·4	12·6	9·6
		$1/2H_2O$	(60·6)	(5·1)	(12·1)	(9·4)
3w	260–261	$C_{18}H_{19}N_3O_2S$	63·3	5·6	12·3	9·4
			(63·1)	(5·5)	(12·3)	(9·4)
3x	231–232	$C_{23}H_{22}N_3O_2S\cdot$	65·4	5·7	10·0	7·6
		H_2O	(65·9)	(5·4)	(9·9)	(7·6)
3y	256–259	$C_{19}H_{21}N_3O_2S$	64·2	5·9	11·8	9·0
			(64·6)	(5·8)	(11·6)	(8·8)

TABLE 2

Absorption Spectral Data of 5-Substituted 2-Thiobarbituric Acid Dyes 3[a] (Solvent: Dimethyl Sulfoxide)

		λ_{max} (*nm*) (*log* ε)											
R	*n*	$R_1 = H, R_2 = H$			$R_1 = H, R_2 = Me$			$R_1 = H, R_2 = Ph$			$R_1 = Me, R_2 = Me$		
MeO	0	**3a**	400	(4·39)	**3b**	403	(4·52)	**3c**	402	(4·34)	**3d**	405	(4·35)
			Δ43[b]			Δ44			Δ45			Δ43	
	1	**3f**	443	(4·65)	**3g**	447	(4·77)	**3h**	447	(4·69)	**3i**	448	(4·73)
			Δ39			Δ36			Δ37			Δ40	
	2	**3j**	482	(4·60)	**3k**	483	(4·74)	**3l**	484	(4·74)	**3m**	488	(4·60)
NMe_2	0	**3n**	496	(4·87)	**3o**	500	(4·89)	**3p**	500	(4·58)	**3q**	502	(4·77)
			Δ77			Δ79			Δ80			Δ82	
	1	**3r**	573	(4·87)	**3s**	579	(4·79)	**3t**	580	(4·86)	**3u**	584	(4·65)
			Δ32			Δ34			Δ31			Δ45	
	2	**3v**	605	(4·37)	**3w**	615	(4·69)	**3x**	611	(4·32)	**3y**	629	(4·44)

[a] **3e** (R = OMe, $n = 0$, $R_1 = R_2 = Ph$): λ_{max} 406 (4·35).

[b] Δ, Difference (nm) between the maxima caused by the increase of *n*.

their application to the colorimetric determination of trace amounts of heavy metal ions more feasible.

3 EXPERIMENTAL

All melting points are uncorrected. UV–visible spectra were recorded on Hitachi 200–10 and Shimadzu 150 spectrophotometers.

p-Methoxyphenylpentadienal (**1c**),[6] *p*-dimethylaminophenylpentadienal (**1f**)[4] and the thiobarbituric acid derivatives[5] were prepared following the reported literature methods.

3.1 Preparation of the Dyes (3a–3y): general procedure

A mixture of **1c** (0·6 mmol) and **2** (R = R′ = Me) in ethanol (9 ml) was refluxed for 1–2 h. The dark green crystals (**3m**) which separated on cooling the reaction mixture were filtered and recrystallized from acetone (87%). Various data of **3m** and of other dyes similarly prepared are given in Tables 1 and 2.

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