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Synthesis and properties of some polycyclic barbiturate pigments

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Abstract

The synthesis, characterisation and properties of some polycyclic barbiturate pigments are described. The pigments have been tested as colourants for plastic and paint and the results of lightfastness, heatfastness and contact bleed tests are reported. Results suggest that only the barbiturate pigments with large aromatic moieties such as the pyren-1-yl and fluoren-2-yl substituents have good lightfastness properties at reduced shades in plastic and only the pyren-1-yl pigment has good lightfastness properties at reduced and full shades in paint. However, all the pigments suffer from poor heatfastness properties in plastic. The absorption coefficient (ε) of some of the pigments is low confirming their weakness in colour strength when tested in high density polyethylene.

Keywords: Pigments; Polycyclic; Barbiturate; Synthesis; Plastic

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1. Introduction

The uses of barbituric acid derivatives are many and varied. In the past, they have been widely used in medical applications as sedative, hypnotic and local anaesthetic drugs [1–5]. However, in recent years, they have been studied as antitumour [6], anticancer [7,8] and anti-osteoporosis agents [9]. They have also been used as disperse dyes with strong fluorescent properties [10], as agrochemical products [11–14] such as insecticides or fungicides, claimed as charge generation agents for electrophotographic photoreceptors [15], studied as non linear optical materials [16] and investigated as stain developers for the identification of nucleic acids [17,18]. Barbituric acid derivatives are also useful in chemical transformations, having been used as organic oxidisers [19], used in the synthesis of unsymmetrical disulfides [20] and as intermediates to oxadeazaflavines [21–24] which are used as biomimetic models of the 5-deazaflavine coenzyme [25–27]. The barbituric acid moiety has also been used effectively in some isoindolinone and azo pigments [28] such as Pigment Yellow 139, 150 and 185 which are used to colour inks, paints and plastics.

Environmental pressures and legislation have gradually seen the decline in use of lead chrome (Pigment Yellow 34) and cadmium pigments (Pigment Yellow 37 and 44) in the plastics and automotive

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paint industry [29]. This has left a gap in the palette of stylists because the excellent properties and shades obtained from these pigments cannot be achieved by the use of the organic pigments alone, presently on the market. The results of this are easy to see. There are few yellow cars on the roads, and those we do see tend to be dull shades. This is because iron oxide or bismuth vanadate pigments have usually been used and these are inherently dull yellows.

Yellow organic pigments such as the isoindolinones Pigment Yellow 109, 110 and 173 are used to a certain extent in the automotive paint industry but on the whole, these suffer from poor durability becoming more intense (darkening) on weathering, especially in full shade [30]. The pigments that are used for industrial vehicles are the diarylide Pigment Yellow 183 and the benzimidazoles Pigment Yellow 151 and 154. These pigments do have the long term durability for use on industrial vehicles which are generally repainted after two years. The copper azomethines Pigment Yellow 117 and 129 are of true automotive quality but are used only in small amounts because they are an unattractive dull greenish yellow and the anthrapyrimidine Pigment Yellow 108 has only a small market because it is weak, very expensive and not completely durable. One method of achieving bright yellow cars is to put down a base coat of bismuth vanadate followed by a benzimidazole or isoindolinone coat and finally a clear coat containing an overdose of UV absorbers. This procedure is extremely expensive and is only used for some sports cars, where auto OEMs tend to work on the safe side having experienced hefty claims in the past for paint failure, in particular due to intercoat adhesion problems.

Yellow is one of the most popular colours in plastics with demand historically met by cadmiums, lead chromes and more recently condensed azos and benzimidazolones. In the plastics industry, the cadmium pigments are no longer used for economic reasons where pigment property requirements such as lightfastness and durability are less strict, eg. polyvinylchloride and low density polyethylene, or for ecological reasons where high demands such as high processing temperatures are made on the pigments in the plastic.

Lead chromate pigment usage dropped significantly in the nineties [31] on health and safety grounds. In the EC, lead chromate pigments are not permitted for use in colouring plastics for consumer goods or coating toys [29]. The concerns over safety of certain pigment types are not only restricted to those based on heavy metals. The future of diarylide pigments in plastics has been called into question because the higher processing temperatures required for certain plastics has led to the thermal decomposition of the pigment leading to unacceptable levels of dichlorobenzidine in the finished product. Unfortunately, as processing temperatures increase, the number of useful, yellow organic pigments used in this application decrease.

Hence, there is a need for high quality, organic yellow pigments with good lightfastness, migration resistance, weather resistance, hiding power and high thermal stability to fill these gaps. Another useful feature for these types of pigment would be to give the plastic good dimensional stability when it is injection moulded.

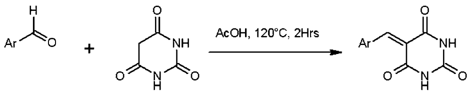
It has been established that organic pigments with the best durability are those with the most efficient packing in the solid state. The most important, intermolecular interactions that contribute to this efficient packing, are π–π stacking and hydrogen bonding [32,33]. The barbituric acid group present in the yellow and orange isoindolinone and azo pigments provides hydrogen bonding within these pigment systems giving them good durability but this still falls short of the standard required for automotive quality. The aromatic component of these pigments and hence the π–π stacking is relatively low compared to pigments with excellent durability and it was reasoned that if this could be increased, it would lead to an increase in durability.

2. Results and discussion

As part of our research efforts into making novel yellow pigments [34,35], our attention focussed on barbiturate pigments due to their simple structures and ease of synthesis. The reaction of simple aromatic aldehydes with barbituric acid by the Knoevnagel condensation under various conditions has been well documented [36–40]. By increasing the aromatic portion of these compounds, it was hoped to prepare pigmentary agents with good durability and enhanced colouristic properties. In this preliminary work, we have been able to prepare pigmentary benzylidene barbituric acid derivatives by reacting polycyclic and substituted aromatic aldehydes (**1**) with barbituric acid as shown in Scheme 1.

The reaction proceeds in glacial acetic acid at reflux for 2 h. This medium provides the necessary acidic nature for catalysis of the Knoevnagel condensation and one in which the products are insoluble even at high temperatures. The pigmentary products are easily isolated in good to excellent yields by filtration and washing, and any reactants or side products remain in solution.

A list of the pigmentary barbituric acids (**3a–l**) prepared, are given in Table 1. Characterisation of the products involved microanalysis and mass spectrometry. The pigments are typically yellow in colour and insoluble in most organic solvents. The absorption spectrum of **3a,b** and **j** in DMF showed peaks between 380 and 440nm and absorption bands of weak intensity (log ε 3.7–4.0), see Table 2. The pigments were tested as colourants for plastics in high density polyethylene (HDPE) and generally found to have poor to good lightfastness properties (2-6 on blue wool scale) in reduced shades. They also gave unacceptable heatfastness results (<220 °C). Typical pigments used in plastics have good lightfastness (6–7) and heatfastness (260 °C and above) properties. All of the barbiturate pigments (**3**) had good contact bleed showing no colour to colour migration problems and some of the barbiturate pigments had similar tinctorials to pigments already used in this type of application. For instance, **3g** gave an attractive yellow similar in hue and strength to the widely used azo Pigment Yellow 93, **3h** gave a slightly dull yellow similar in hue and strength to the isoindolinone Pigment Yellow 109 and **3l** gave a reasonably attractive yellow very similar in hue



Scheme 1. Synthesis of barbiturates **3a–l**.

Table 2
Absorption properties of barbiturate pigments

Pigment	λ_{max} nm	ε dcm^3/mol cm
3a	436	6475
3b	384	10325
3j	398	5390

Table 1
Yields and test properties in HDPE of barbituric pigments

Pigment	Ar	Yield%	Plastic Colouration	Light Fastness[b]	Heat fastness °C	Contact bleed[c]
3a	Pyren-1-yl	94	Orange shade red	6	<200	5
3b	Fluoren-2-yl	90	Weak, greenish yellow	5	<200	5
3c	Benzo[1,3]dioxol-5-yl	91	Weak, green shade yellow	4	<200	5
3d	Phenanthren-9-yl	76	Weak yellow	2	<200	5
3e	3,4-Dichlorophenyl	70	Weak yellow	[a]	<200	5
3f	4-Biphen-1-yl	81	Very weak yellow	[a]	<200	5
3g	Benzofuran-2-yl	86	Strong, green shade yellow	2	<200	5
3h	Indol-3-yl	76	Weak, green shade yellow	6	200	5
3i	Chromon-3-yl	75	[a]	[a]	[a]	[a]
3j	10-Chloroanthracen-9-yl	45	Weak, dull red/violet	2	220	5
3k	Naphth-2-yl	75	Very weak yellow	2	<200	5
3l	Naphth-1-yl	72	Green shade yellow	2	<200	5

[a] Not tested.

[b] For reduced shade in HDPE.

[c] Scale 1-Poor, 5-Excellent.

and strength to the azo calcium toner Pigment Yellow 168. Further testing of the promising barbiturates **3a, b** and **h** in paints (see Table 3) revealed that only **3a** had good lightfastness properties in both reduced and full shade although it did have unacceptable durability (3–4) as it darkened on exposure in the xenon lightfastness test.

The poor lightfastness properties of these pigments may be due to the styryl double bond between the polycyclic aromatic moiety and the barbiturate group. Strengthening the double bond by eliminating the abstractable hydrogen atom could be achieved by incorporation of an aryl or alkyl substituent at this position. Reaction of ketones with barbituric acid presents us with a whole, new problem and this work will be reported later.

3. Experimental

3.1. General

Unless otherwise stated, all chemicals were purchased from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification. Fluorene-2-carboxaldehyde and chromone-3-carboxaldehyde were purchased from Lancaster Synthesis. Melting points were determined on a Gallenkamp melting point apparatus. UV/Visible spectra were measured on a Pye Unicam Helios Alpha spectrophotmeter. Mass spectra and microanalytical determinations were performed by Avecia Analytical Sciences Group on a Micromass Platform II instrument and a Leco 932 C H N S analyser respectively. Lightfastness results were obtained using an air cooled Xenon Arc Fading Tester 150.

Table 3
Properties of pigments in paint

Pigment	Light fastness reduced shade	Light fastness full shade	Overspray fastness	Colour
3a	6	6	5	Yellow shade red
3b	1	[a]	5	Green shade yellow
3h	1	[a]	5	Yellow

[a] Not tested.

3.2. Synthesis of barbiturate pigments 3a–l

The polycyclic aromatic aldehyde (10 mmols) and barbituric acid (11 mmols) were stirred in glacial acetic acid (30 ml) at reflux for 2 h. The precipitated solid was filtered off from the hot solution and washed consecutively with more glacial acetic acid (30 ml), then water (50 ml) and finally dried in an oven at 60 °C to give the barbiturate pigment. Yields are given in Table 1.

5-Pyren-1-ylmethylene-pyrimidine-2,4,6-trione **3a** was isolated as a red solid, m.p. >300 °C. Elemental analysis, calculated for $C_{21}H_{12}N_2O_3$: C, 74.1; H, 3.55; N 8.25. Found: C, 74.6; H, 3.4; N, 8.1.

5-Fluoren-2-ylmethylene-pyrimidine-2,4,6-trione **3b** was isolated as a fluorescent, red shade yellow solid, m.p. >300 °C; *m/z* 304 (M^+, 100%). Elemental analysis, calculated for $C_{18}H_{12}N_2O_3$: C, 71.05; H, 4.0; N, 9.2. Found: C, 71.2; H, 4.1; N, 9.4.

5-Benzo [1,3] dioxol-5-ylmethylen-pyrimidine-2,4,6-trione **3c** was isolated as a yellow solid, m.p. >300 °C. Elemental analysis, calculated for $C_{12}H_8N_2O_5$: C, 55.4; H, 3.1; N, 10.75. Found: C, 56.0; H, 3.1; N, 10.8.

5-Phenanthren-9-ylmethylene-pyrimidine-2,4,6-trione **3d** was isolated as an orange solid, m.p. >300 °C. *m/z* 315 (M^+–H, 5%). Elemental analysis, calculated for $C_{19}H_{12}$ N_2O_3: C, 72.15; H, 3.8; N, 8.85. Found: C, 72.3; H, 4.0; N, 9.0.

5-(3,4-Dichlorophen-1-yl)methylene-pyrimidine-2,4,6-trione **3e** was isolated as a yellow solid, m.p. >300 °C; *m/z* 284 (M^+, 100%). Elemental analysis, calculated for $C_{11}H_6Cl_2N_2O_3$: C, 46.35; H, 2.1; N, 9.8; Cl 24.85. Found: C, 46.7; H, 2.3; N, 9.7; Cl, 25.3.

5-(4-Biphen-1-yl)methylene-pyrimidine-2,4,6-trione **3f** was isolated as a pale yellow solid, m.p. >300 °C; *m/z* 292 (M^+, 100%), 248 (20). Elemental analysis, calculated for $C_{17}H_{12}N_2O_3$: C, 69.85; H 4.15; N 9.6. Found: C, 69.5; H, 4.2; N, 9.5.

5-Benzofuran-2-ylmethylene-pyrimidine-2,4,6-trione **3g** was isolated as a red shade yellow solid, m.p. >300 °C; *m/z* 255 (M^+-H, 10%). Elemental analysis, calculated for $C_{13}H_8N_2O_4$: C, 60.95; H, 3.15; N, 10.95. Found: C, 61.4; H, 3.3; N, 11.0.

5-Indol-3-ylmethylene-pyrimidine-2,4,6-trione **3h** was isolated as a red shade yellow solid, m.p. >300 °C; *m*/*z* 254 (M^+- H, 50%). Elemental analysis, calculated for $C_{13}H_9N_3O_3$: C, 61.2; H, 3.55; N, 16.45. Found: C, 61.3; H, 3.3; N, 16.3.

5-Chromon-3-ylmethylene-pyrimidine-2,4,6-trione **3i** was isolated as a yellow solid, m.p. >300 °C; *m*/*z* 283 (M^+- H, 5%). Elemental analysis, calculated for $C_{14}H_8N_2O_5$: C, 59.15; H, 2.85; N, 9.85. Found: C, 59.6; H, 2.5; N, 9.9.

5-(10-Chloroanthracen-9-yl)methylene-pyrimidine-2,4,6-trione **3j** was isolated as a red solid, m.p. >300 °C; *m*/*z* 349 (M^+−H, 7%). Elemental analysis, calculated for $C_{19}H_{11}ClN_2O_3$: C, 65.05; H, 3.15; N, 8.0; Cl, 10.1. Found: C, 64.8; H, 3.2; N, 8.0; Cl, 11.0.

5-Naphth-2-ylmethylene-pyrimidine-2,4,6-trione **3k** was isolated as a green shade yellow solid, m.p. >300 °C; *m*/*z* 265 (M^+−H, 3%). Elemental analysis, calculated for $C_{15}H_{10}N_2O_3$: C, 67.65; H, 3.8; N, 10.5. Found: C, 67.3; H, 3.8; N, 10.4.

5-Naphth-1-ylmethylene-pyrimidine-2,4,6-trione **3l** was isolated as a green shade yellow solid, m.p. >300 °C; *m*/*z* 265 (M^+- H, 5%). Elemental analysis, calculated for $C_{15}H_{10}N_2O_3$: C, 67.65; H, 3.8; N, 10.5. Found: C, 67.8; H, 3.9; N, 10.5.

3.3. Testing of barbiturate pigments in HDPE Plastic at reduced shade

The barbiturate pigment (1.5 g), titanium dioxide (15 g TiO_2 R-FC5, ex Huntsman rutile grade) and HDPE granules (1483.5 g ATO 2070 MN60, ex Ashland Plastics, MFR 7) were mixed in a Henschel mixer (1800 rpm) at room temperature for 2×30 s periods. This mixture was then fed into a twin screw extruder (Boy 22S) and extruded at 190–200 °C. The coloured masterbatch was moulded into plaques of 5 cm by 2.5 cm tablets of 2 mm thickness at 200 °C.

3.4. Method of paint manufacture in alkyd MF resin paint system

3.4.1. Millbase

Glass beads (3 mm) (125 g) were weighed into a 140 ml screw cap bottle. Into this, 20% Crodakyd 130X/70 (ex Croda Resins) in 4:1 xylene:butanol (25 g) and the barbiturate pigment (5.3 g) were added. The bottle was shaken by hand until homogeneous and then shaken on a Red Devil shaker for 30 min. The seed/bit level was noted and found to be off-gauge. The millbase was allowed to cool to room temperature.

3.4.2. Letdown

Into the tared 140 ml glass bottle was added 70% Crodakyd 130X/70 (ex Croda Resins) (45.9 g) carefully as follows: 2, 4, 8, 16 g etc. After each addition the bottle was shaken vigorously. Then, approximately half of the millbase contents were transferred to a 280 ml bottle without the beads and the letdown was continued with addition of 60% Beetle BE 615 resin (ex BP Chemicals) (26.5 g) and xylene (3.3 g) into the 140 ml bottle. The 140 ml bottle was shaken by hand and then all the contents including the beads were poured into the 280 ml bottle which was shaken to ensure homogeneity. The paint was checked visually to make sure shock seeding had not occurred. The total paint weight is 106 g and the pigment content is 5% with a Pigment/Binder ratio of 0.1/1 and a pigment/resin solution ratio of 17.5/82.5.

3.4.3. Full shade

Full shade patterns were obtained by drawdown on black/white card by means of a 250 micron bar. The paint was allowed to air dry for 15 mins and then stoved at 120 °C for 30 min. Lightfastness/overspray fastness properties were assessed from these patterns.

3.4.4. Reduced shade

Into a 70 ml screw cap bottle, the coloured paint (8.0 g) and a white alkyd/MF stoving enamel (ex Avecia) (TiO_2 content 25%) was added. The contents were mixed thoroughly by rolling on a mill until the mixture is visually homogeneous. The reduced shade paints were sprayed on white card (Spray booth/gun AGG-500 series ex De Vilbiss co), allowed to dry for 15 mins and then stoved in an oven at 120 °C for 30 min. Lightfastness/overspray fastness properties were assessed from these patterns.

3.5. Assessment and measurement of plastic plaques and paint patterns

3.5.1. Overspray fastness

Full and reduced shade paint patterns were sprayed over with the white alkyd/MF stoving enamel (ex Avecia) (TiO_2 content 25%) until full hide was achieved. These patterns were then stoved in an oven at 120 °C for 30 min. The bleed into the white overspray patterns were assessed using the 1–5 International Grey Scale based on ISO 105 A03 (1994) for assessing staining by comparison with the corresponding white finish as control, 1 being least fast showing colour migration/staining into the top white coat and 5 being fully overspray fast showing no colour migration.

3.5.2. Light fastness

The HDPE plaques and Full/Reduced shade paint patterns were exposed to light in a Xenon arc tester until a fade could be detected using the British standard BS EN 20105-B02 (1993) Annex A, blue wool scale (1–8), 1 being least fast, 8 being fully light fast indicating no discernible change.

3.5.3. Contact bleed (Migration resistance)

A plaque of the pigmented polymer (0.5% colour pigment and 1% titanium dioxide) is placed in contact with a similar plaque of polymer containing only titanium dioxide (1%) at 50 °C for 3 days. Any stain on the plaque containing no coloured pigment is then assessed using the International Grey Scale (1–5) based on ISO 105 A02 (1993) where a rating of 5 indicates no stain.

3.5.4. Heat stability

Heat stability of the pigments was evaluated over the temperature range 200–300 °C in steps of 20 °C preparing plaques at each temperature in mouldings after a 10 min dwell time in the extruder barrel. The control plaque was prepared from a short 20 s cycle at 200 °C. Differences in colour of each plaque compared to the control were measured (CIELAB) and the maximum temperature at which δ E does not exceed 1.7 (CIELAB) (which is equivalent to a Grey Scale rating of 4, ISO 105 A02) was recorded as the heat stability.

4. Conclusions

A simple procedure for the synthesis of polycyclic barbiturates has been described. These pigmentary products have been obtained in good yield with minimal purification. 5-Pyren-1-ylmethylene-pyrimidine-2,4,6-trione (**3a**) has the best lightfastness properties of the whole group when tested as a colorant in plastics and paint. Most of the barbiturate pigments suffer from poor lightfastness and heatfastness properties when incorporated into HDPE.

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