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The crystal and molecular structures of three diarylide yellow pigments, C. I. Pigments Yellow 13, 14 and 63

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Abstract

All three pigments crystallise in the triclinic system, space group $P\bar{1}$, and with one molecule in the unit cell so that all molecules have crystallographic C_i symmetry. The molecules exist in the bisketohydrazone tautomeric form. The *intra*molecular hydrogen bonding normally associated with this structural arrangement is observed, but there is no *inter*molecular hydrogen bonding. The molecules are not quite planar, but deviate from planarity by only a few degrees of torsional bond rotations. In each structure the molecules pack together in inclined interleaved stacks so that the ketohydrazonoarylamide groups lie above and below one another in antiparallel arrangements. The colour and technical performance of the pigments are discussed in relation to the structural details.

Keywords: X-ray crystallography; C. I. Pigment Yellow 13; C. I. Pigment Yellow 14; C. I. Pigment Yellow 63; Disazoacetoacetanilide; Diarylide yellow; Disazo pigment; Ketohydrazone

1. Introduction

The most important yellow classical organic pigments are a series of disazoacetoacetanilides, commonly referred to as the Diarylide Yellows [1–4]. Although frequently illustrated in the literature as disazo structures, it has been demonstrated that they exist exclusively in the bisketohydrazone tautomeric form (**1**) both in solution and in solid state phases [5]. The chemical structures of the most important commercial products in the series are shown in Table 1. These pigments are invariably symmetrically-substituted compounds, synthesised by azo coupling of a tetrazotised benzidine derivative, most commonly 3,3′-dichlorobenzidine (1 mol) with an acetoacetanilide coupling component (2 mol). The pigments are structurally analogous to the monoazoacetoacetanilides (Hansa Yellows) of which C. I. Pigment Yellow 1 (Y1) is a typical example and one of the most important commercial products.

The monoazo pigments, such as Y1, are characterised by bright yellow colours of moderate intensity, and good lightfastness but rather poor resistance towards organic solvents. They tend therefore to be used in applications such as water-based decorative paints where this deficiency is not critical. The disazo pigments Y12, Y13, Y14 and

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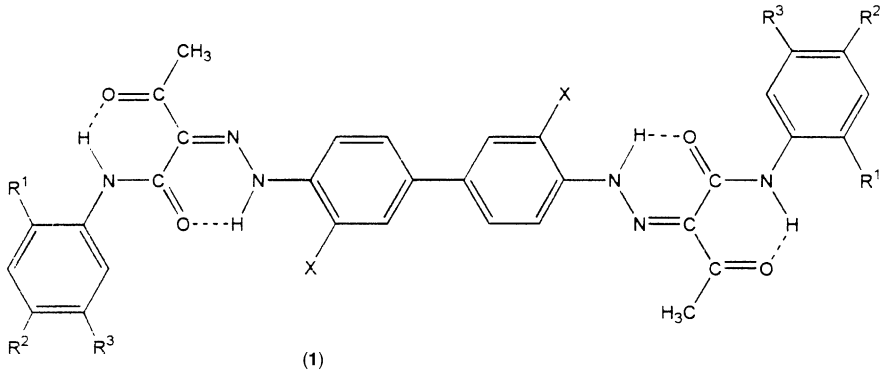

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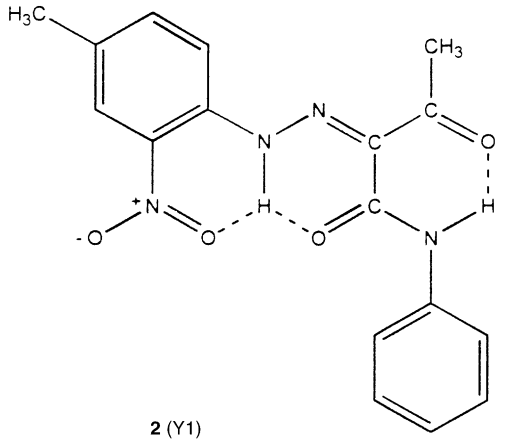

2 (Y1)

Table 1
The substituent pattern in industrially important disazoacetoacetanilide pigments

Compound	C.I. Pigment	R^1	R^2	R^3	X
1a (Y12)	Yellow 12	H	H	H	Cl
1b (Y13)	Yellow 13	CH_3	CH_3	H	Cl
1c (Y14)	Yellow 14	CH_3	H	H	Cl
1d	Yellow 17	OCH_3	H	H	Cl
1e	Yellow 55	H	CH_3	H	Cl
1f (Y63)	Yellow 63	Cl	H	H	Cl
1g	Yellow 83	OCH_3	Cl	OCH_3	Cl
1h	Orange 16	H	H	H	OCH_3

Y63 also provide bright yellow colours together with higher colour strength, higher transparency and improved solvent resistance compared with the monoazo pigments, but they have inferior lightfastness. These features, together with their relatively low cost, mean that they are particularly suited to printing ink applications and they are in fact the dominant yellow pigments used for this purpose. Y12 has inferior colour strength, lightfastness and solvent resistance compared with the others in the series, but is used extensively because it is the lowest cost product. Y13 is the most significant product in the series and is arguably the most important of all yellow organic pigments. It provides the mid-shade yellow of the European standard for four-colour process printing, high transparency, and an optimum balance of fastness properties with cost. Y14 and Y63 are also used in the coloration of printing inks, although the latter is of limited importance because of inferior lightfastness.

Organic pigments are applied as discrete crystalline solid particles, retained mechanically in their application within a polymeric matrix. Their performance in terms of optical properties (including colour and transparency) and fastness properties (for example to light, heat and solvents) are thus dependent not only on their molecular structure but also on solid state characteristics (including particle size and shape distribution and the three-dimensional crystallographic arrangement of the pigment molecules). X-ray single crystal structural studies on pigments are thus of importance in determining the crystallographic arrangement, including details of the intramolecular and intermolecular interactions. Such information assists understanding the technical performance of the products and is an essential first stage in the crystal engineering of new products, the utilisation of such understanding in the design of new solids with desired physical and chemical properties.

The crystal structures of a number of monoazoacetoacetanilide pigments have been established and the results reviewed [6]. Crystal structure determinations of Y1 [7–9] have shown that the molecule exists as a ketohydrazone with bifurcated *intra*molecular hydrogen bonding involving the *ortho* nitro group and the amide group as illustrated. The Y1 molecule is approximately planar although with some other derivatives there is a twisting of up to 20° of the anilide phenyl ring, and in most cases the molecules are stacked in columns in an antiparallel arrangement [6]. It was rather surprising to us that no comparable single-crystal X-ray studies on the industrially more important Diarylide yellow pigments had been published and thus, some time ago, we initiated a programme of research, in collaboration with Ciba Pigments (now part of the Ciba Speciality Chemicals organisation), to elucidate the crystal structures of several of these pigments and to investigate relationships with their colouristic and technical performance. We recently published the X-ray single crystal structure of Y12, the first investigation in the series [10]. In this paper, we now report the X-ray single crystal structures of three further derivatives,Y13, Y14 and Y63.

2. Experimental

2.1. Synthesis and crystallisation

C. I. Pigment Yellow 13, 2,2′-[(3,3′-dichloro[1,1′-biphenyl]-4,4′-diyl)bis(azo)bis[*N*-(2,4-dimethylphenyl)-3-oxo-butanamide], C. I. Pigment Yellow 14, 2,2′-[(3,3′-dichloro[1,1′-biphenyl]-4,4′-diyl)bis(azo)-bis[*N*-(2-methylphenyl)-3-oxo-butanamide] and C. I. Pigment Yellow 63, 2,2′-[(3,3′-dichloro[1,1′ -biphenyl]-4,4′-diyl)bis(azo)bis[*N*-(2-chlorophenyl)-3-oxo-butanamide] were prepared by tetrazotisation of 3,3′-dichlorobenzidine, followed by azo coupling of the resulting tetrazonium salt with the appropriate acetoacetanilide coupling components using well-established procedures [5]. All three pigments are highly insoluble in organic solvents at room temperatures, but it was found that they had sufficient solubility in 1,2,4-trichlorobenzene around its boiling point to enable single crystals suitable for X-ray analysis to be grown from solutions of the pigments, contained in sealed tubes, by slow cooling from 200 °C over a period of several days.

2.2. Crystal structure determination

Single crystals of the pigments were examined by X-ray photography (12 crystals for Y13, 7 for Y14 and 4 for Y63). In each case three crystals were selected for X-ray diffractometer measurements. Crystal 1 was mounted along the *a* axis, crystal 2 along the *b* axis and crystal 3 along the *c* axis. Space groups and approximate cell parameters were obtained from oscillation and Weissenberg photographs (Cu K_α radiation). Intensity data and accurate cell parameters (from 2θ and ω setting angles) were measured using a Stoe Stadi-2 two-circle diffractometer (Mo K_α radiation, graphite monochromator).

2.2.1. Crystal data

2.2.1.1. C. I. Pigment Yellow 13. $C_{36}H_{34}Cl_2N_6O_4$, $M_r = 685.59$; intense orange crystals; triclinic; $a = 8.363(4)$, $b = 12.512(8)$, $c = 8.743(7)$ Å; $\alpha = 71.68(2)$, $\beta = 105.70(8)$, $\lambda = 104.04(4)°$; $V = 823.5$ Å^3; space group $P\bar{1}$; $Z = 1$; $D_x = 1.35$ Mg m^{-3}; $D_c = 1.41$ Mg m^{-3}; $T = 295$ K; $\lambda = 0.71073$ Å (Mo K_α radiation); $\mu = 0.25$ mm^{-1}. Cell parameters from 18 $0kl$ reflections ($19° < 2\theta < 26°$) from crystal 1, 18 $h0l$ reflections ($20° < 2\theta < 31°$) from crystal 2, and 18 $hk0$ reflections ($12° < 2\theta < 21°$) from crystal 3. 6259 reflections measured from layers $0 \rightarrow 4$, k, l; h, $0 \rightarrow 2$, l; h, k, $0 \rightarrow 9$; 3470 unique reflections giving 1799 with $I > 3\sigma(I)$; $R = 0.036$ and $R_w = 0.046$. Final weighting scheme $w = 1/[1 + 0.02(8 - F_o)^2]$ for $F_o < 8$ and $w = 1/[1 + 0.008(F_o - 8)^2]$ for $F_o > 8$. Final $\Delta\rho = \pm 0.22$ e Å^{-3}.

2.2.1.2. C. I. Pigment Yellow 14. $C_{34}H_{30}Cl_2N_6O_4$, $M_r = 657.55$; intense orange crystals; triclinic; $a = 8.209(5)$, $b = 13.352(5)$, $c = 9.331(6)$ Å; $\alpha = 120.21(2)$, $\beta = 74.57(6)$, $\lambda = 119.23(4)°$; $V = 771.0$ Å^3; space group $P\bar{1}$; $Z = 1$; $D_x = 1.41$ Mg m^{-3}; $D_c = 1.44$ Mg m^{-3}; $T = 295$ K; $\lambda = 0.71073$ Å (Mo K_α radiation); $\mu = 0.262$ mm^{-1}. Cell parameters from 20 $0kl$ reflections ($19° < 2\theta < 25°$) from crystal 1, 20 $h0l$ reflections ($21° < 2\theta < 25°$) from crystal

2, and 24 *hk*0 reflections ($17° < 2\theta < 24°$) from crystal 3. 5937 reflections measured from layers 0 → 5, *k*, *l* and *h*, *k*, 0 → 9; 3460 unique reflections giving 2064 with $I > 3\sigma(I)$; $R = 0.033$ and $R_w = 0.043$. Final weighting scheme for all reflections $w = 1/[1 + 0.008(F_o - 8)^2]$. Final $\Delta\rho = \pm 0.21$ e Å^{-3}.

2.2.2. C. I. Pigment Yellow 63

$C_{32}H_{24}Cl_4N_6O_4$, $M_r = 698.39$; yellow plate-shaped crystals; triclinic; $a = 8.095(3)$, $b = 11.728(3)$, $c = 9.099(3)$ Å; $\alpha = 67.61(10)$, $\beta = 76.72(3)$, $\lambda = 96.74(3)°$; $V = 757.0$ Å^3; space group $P\bar{1}$; $Z = 1$; $D_x = 1.23$ Mg m^{-3}; $D_c = 1.53$ Mg m^{-3}; $T = 295$ K; $\lambda = 0.71073$ Å (Mo K_α radiation); $\mu = 0.262$ mm^{-1}. Cell parameters from 28 *h*0*l* reflections ($8° < 2\theta < 34°$) from crystal 2, and 30 *hk*0 reflections ($11° < 2\theta < 32°$) from crystal 3. Crystal 1, aligned along the *a* axis, was used only for photographic determination of α^*. 3285 reflections measured from layers 0, *k*, *l* and *h*, *k*, 0 → 9; 3107 unique reflections giving 1463 with $I > 3\sigma(I)$; $R = 0.038$ and $R_w = 0.047$. Final weighting scheme for all reflections $w = 1/[1 + 0.00074(F_o - 10)^2]$. Final $\Delta\rho = \pm 0.4$ e Å^{-3}.

Intensity data were corrected for Lorentz and polarisation effects and, for Y63 only, absorption corrections were also calculated and applied using SHELX76 [11]. Structure solutions were by direct methods (SHELXS86 [12]) and structure refinements by least squares (SHELX76) to minimise $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atoms were included with isotropic parameters; all other atom types had anisotropic parameters. All hydrogen atoms were located from difference Fourier syntheses and their parameters refined. However, the methyl hydrogens attached to C9 (Y13 and Y14) and to C18 (Y13) had to be held at fixed positions, corresponding to the positions of maximum local electron density, in order to achieve convergence in the final cycles of least-squares calculations. This suggests some rotational motion about the C–CH_3 bonds in those cases.

3. Results and discussion

The crystal structures of the three pigments are very similar to one another, but they are different in several respects from that of Y12 [10]. The molecular structures of Y13, Y14 and Y63 differ only in the substitution pattern in the terminal anilide rings, Y12 being the parent unsubstituted compound. Y13, Y14 and Y63 each have a single *ortho* substituent (methyl in the case of Y13 and Y14, chloro in the case of Y63) and, additionally, Y13 contains a *para*-methyl group. A comparison of the crystal structure data for the range of pigments discussed in this paper provides some clarification of the influence of crystal structure properties on their colouristic and technical performance.

Fig. 1a–c shows the molecular structures and indicate the atomic labelling schemes. Atomic parameters and derived geometrical quantities are given in Tables 2–5. The crystal structure determinations confirm that the molecules exist in the bisketohydrazone tautomeric form, similar to Y12 and analogous to the closely-related monoazoacetacetanilide pigments [6]. Important bond lengths which may be highlighted in this respect are the N–N (1.308–1.321 Å), the hydrazone C-N (1.305–1.313 Å), the ketone C=O (1.217–1.221 Å) and amide C=O (1.223–1.233 Å), which are comparable with the bond lengths reported for Y12 and for the range of monoazo analogues. In each of pigments Y13, Y14 and Y63, the crystallographic asymmetric unit is a half molecule, the two halves being related by a crystallographic centre of symmetry located midway between C1 and C1′ (the biphenyl linkage). This symmetry means that the two benzene rings (C1–C6 and C1′–C6′) which constitute the biphenyl system must be parallel to one another, although not necessarily coplanar. In the case of Y13, one phenyl ring lies slightly (0.05 Å) above the plane of the other. However, in Y14 and Y63 the two rings of the biphenyl system are, in fact, coplanar. In this respect, these three pigments differ from Y12 in which there is no crystallographically-imposed molecular symmetry and where there is a torsional rotation about the C1–C1′ biphenyl linkage of 27° [10]. Each half molecule in the structures of Y13, Y14 and Y63 is slightly internally twisted so that the plane of the terminal (anilide) benzene ring makes a small dihedral angle with the plane of the biphenyl ring (C1–C6). With Y13 this dihedral

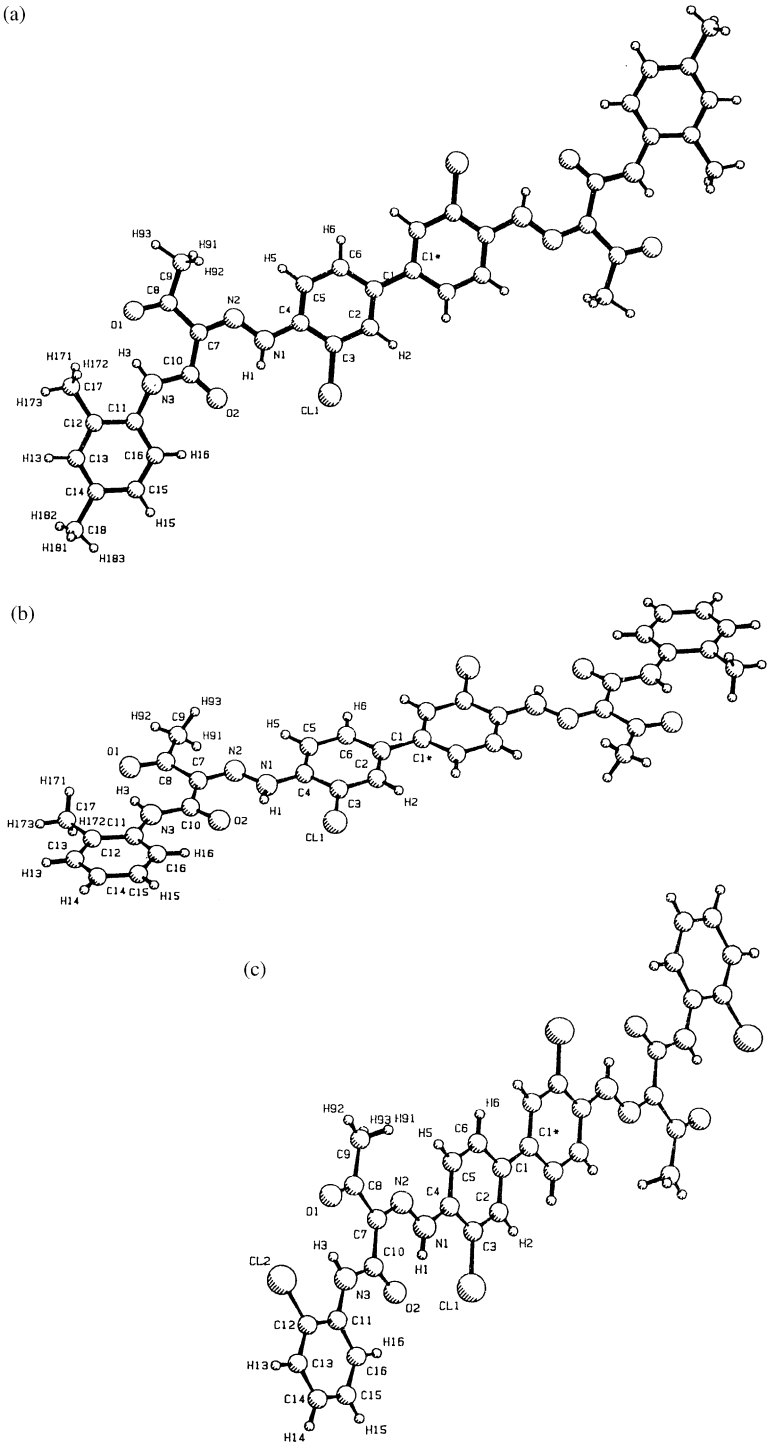

Fig. 1. Molecular structure of (a) Y13, (b) Y14 and (c) Y63 with atomic numbering scheme.

Table 2
Atomic parameters (e.s.d.s in parentheses)

Atom	x/a	y/b	z/c	U_{eq} / U_{iso}
(a) *Y13*				
CL1	0.33212(11)	0.23015(8)	0.14117(10)	0.0578(5)
O1	−0.31698(26)	0.57807(18)	−0.37892(28)	0.0544(14)
O2	0.16256(23)	0.48599(16)	−0.21416(23)	0.0430(11)
N1	0.01804(30)	0.32856(19)	0.00355(26)	0.0369(12)
N2	−0.11958(27)	0.37400(17)	−0.06858(26)	0.0356(12)
N3	−0.00245(30)	0.60458(19)	−0.41257(27)	0.0373(13)
Cl	0.00228(36)	0.04824(22)	0.42416(31)	0.0375(15)
C2	0.14466(40)	0.08869(24)	0.35652(33)	0.0429(16)
C3	0.14881(35)	0.18071(24)	0.21796(32)	0.0397(15)
C4	0.01056(34)	0.23498(22)	0.14092(29)	0.0356(14)
C5	−0.13361(38)	0.19354(24)	0.20607(34)	0.0431(16)
C6	−0.13674(40)	0.10281(25)	0.34464(35)	0.0439(16)
C7	−0.12318(32)	0.46116(21)	−0.19870(31)	0.0354(14)
C8	−0.29009(36)	0.49753(24)	−0.25845(36)	0.0438(16)
C9	−0.42743(40)	0.43341(29)	−0.16594(44)	0.0575(21)
C10	0.02608(33)	0.51812(21)	−0.27536(30)	0.0340(14)
C11	0.11140(34)	0.67834(21)	−0.50959(31)	0.0346(14)
C12	0.04500(33)	0.76150(22)	−0.64736(31)	0.0355(14)
C13	0.15465(38)	0.83581(23)	−0.74300(34)	0.0396(15)
C14	0.32430(38)	0.83135(24)	−0.70858(35)	0.0450(17)
C15	0.38568(39)	0.74924(26)	−0.57208(38)	0.0478(18)
C16	0.28178(35)	0.67338(25)	−0.47322(36)	0.0426(16)
C17	−0.13816(40)	0.77046(30)	−0.69048(42)	0.0466(18)
C18	0.43621(48)	0.91297(30)	−0.82102(46)	0.0660(23)
H1	0.109(4)	0.360(3)	−0.037(4)	0.058(9)
H2	0.248(4)	0.052(2)	0.404(4)	0.053(9)
H3	−0.110(4)	0.616(2)	−0.441(4)	0.050(9)
H5	−0.231(4)	0.230(3)	0.157(4)	0.056(9)
H6	−0.238(4)	0.081(2)	0.385(3)	0.044(8)
H13	0.104(3)	0.889(2)	−0.837(3)	0.042(7)
H15	0.501(4)	0.744(3)	−0.548(4)	0.057(9)
H16	0.324(4)	0.619(3)	−0.386(4)	0.051(8)
H91	−0.400	0.450	−0.060	0.090
H92	−0.440	0.350	−0.170	0.090
H93	−0.540	0.470	−0.230	0.090
H171	−0.174(4)	0.784(3)	−0.601(4)	0.065(10)
H172	−0.208(4)	0.701(3)	−0.715(4)	0.068(10)
H173	−0.161(4)	0.831(3)	−0.778(4)	0.067(10)
H181	0.420	0.880	−0.905	0.090
H182	0.430	0.985	−0.810	0.090
H183	0.550	0.905	−0.760	0.090
(b) *Y14*				
CL1	−0.09027(9)	0.26297(7)	0.38321(10)	0.05587(46)
O1	0.89520(21)	0.59902(16)	0.17055(24)	0.0548(11)
O2	0.32773(20)	0.51938(16)	0.26534(23)	0.0486(11)
N1	0.31929(25)	0.34929(17)	0.32614(23)	0.0388(10)
N2	0.49971(24)	0.39065(16)	0.29215(22)	0.0391(10)
N3	0.60656(25)	0.63926(16)	0.17839(23)	0.0387(10)
C1	0.04873(29)	0.05208(19)	0.47342(26)	0.0369(11)
C2	−0.05009(32)	0.10378(21)	0.45270(28)	0.0405(13)
C3	0.04054(30)	0.20080(20)	0.40378(27)	0.0396(12)
C4	0.23191(28)	0.24996(19)	0.37290(26)	0.0377(12)
C5	0.33116(31)	0.19785(21)	0.39167(30)	0.0433(13)
C6	0.24116(32)	0.10161(21)	0.44124(30)	0.0438(14)
C7	0.58889(27)	0.48280(18)	0.24645(25)	0.0361(11)
C8	0.79101(30)	0.51418(21)	0.21214(30)	0.0456(13)
C9	0.86525(42)	0.43914(34)	0.23113(54)	0.0605(21)
C10	0.49555(27)	0.54859(19)	0.23089(26)	0.0379(12)
C11	0.56296(28)	0.72189(19)	0.15915(25)	0.0369(11)
C12	0.70973(30)	0.80832(20)	0.10243(27)	0.0407(12)
C13	0.67093(38)	0.89144(23)	0.08379(33)	0.0509(15)
C14	0.49739(40)	0.89093(25)	0.11890(36)	0.0574(18)
C15	0.35568(39)	0.80504(26)	0.17270(35)	0.0570(17)
C16	0.38735(32)	0.72091(23)	0.19343(31)	0.0472(14)
C17	0.90073(34)	0.81119(28)	0.06345(41)	0.0508(16)
H1	0.261(4)	0.386(2)	0.322(3)	0.058(8)
H2	−0.182(3)	0.076(2)	0.471(3)	0.046(6)
H3	0.726(4)	0.649(2)	0.166(3)	0.061(7)
H5	0.464(4)	0.233(2)	0.375(3)	0.055(7)
H6	0.316(3)	0.073(2)	0.455(3)	0.045(6)
H13	0.767(4)	0.947(2)	0.039(3)	0.060(7)
H14	0.479(4)	0.950(2)	0.106(3)	0.065(7)
H15	0.238(4)	0.808(3)	0.202(3)	0.078(9)
H16	0.291(3)	0.665(2)	0.228(3)	0.050(6)
H91	0.798(5)	0.356(3)	0.184(4)	0.094(11)
H92	0.989(5)	0.465(3)	0.202(4)	0.096(11)
H93	0.842(5)	0.450(4)	0.348(5)	0.123(14)
H171	0.962(4)	0.831(3)	0.155(4)	0.082(10)
H172	0.898(4)	0.725(3)	−0.031(4)	0.082(9)
H173	0.982(4)	0.872(3)	0.029(3)	0.081(9)
(c) *Y63*				
CL1	0.35925(15)	0.26746(13)	0.60855(19)	0.0492(9)
CL2	−0.12132(16)	0.82126(12)	0.94847(17)	0.0458(8)
O1	−0.3072(4)	0.6024(3)	0.8347(5)	0.048(2)
O2	0.1883(4)	0.5286(3)	0.7302(5)	0.043(2)
N1	0.0289(5)	0.3527(3)	0.6748(5)	0.034(2)
N2	−0.1120(5)	0.3930(3)	0.7117(4)	0.035(2)
N3	0.0247(5)	0.6466(3)	0.8242(5)	0.033(2)
C1	0.0042(5)	0.0528(4)	0.5267(5)	0.030(2)
C2	0.1563(6)	0.1064(4)	0.5429(6)	0.034(3)
C3	0.1626(5)	0.2032(4)	0.5936(5)	0.031(2)
C4	0.0173(5)	0.2517(4)	0.6289(5)	0.031(3)
C5	−0.1356(6)	0.1981(4)	0.6137(6)	0.036(3)
C6	−0.1426(6)	0.1008(4)	0.5653(6)	0.037(3)
C7	−0.1113(5)	0.4864(4)	0.7575(5)	0.031(2)
C8	−0.2859(6)	0.5166(4)	0.7937(6)	0.041(3)
C9	−0.4351(7)	0.4388(5)	0.7785(8)	0.054(4)
C10	0.0481(6)	0.5556(4)	0.7681(5)	0.032(2)
C11	0.1518(6)	0.7295(4)	0.8398(5)	0.033(3)
C12	0.0982(6)	0.8176(4)	0.8983(5)	0.034(3)
C13	0.2149(7)	0.9026(5)	0.9162(6)	0.044(3)
C14	0.3902(7)	0.9012(5)	0.8775(7)	0.051(4)
C15	0.4447(7)	0.8145(5)	0.8228(7)	0.050(3)
C16	0.3282(6)	0.7290(4)	0.8036(6)	0.041(3)
H1	0.121(6)	0.385(4)	0.688(5)	0.036(13)
H2	0.259(6)	0.077(4)	0.524(6)	0.052(13)
H3	−0.082(7)	0.652(5)	0.846(6)	0.064(17)
H5	−0.235(6)	0.233(4)	0.629(5)	0.049(13)
H6	−0.245(5)	0.074(4)	0.550(5)	0.040(12)
H13	0.173(6)	0.956(4)	0.963(6)	0.060(14)
H14	0.471(5)	0.956(4)	0.897(5)	0.041(12)
H15	0.560(6)	0.808(4)	0.801(6)	0.050(14)
H16	0.362(5)	0.672(4)	0.764(5)	0.042(12)
H91	−0.419	0.437	0.676	0.080
H92	−0.535	0.459	0.793	0.080
H93	−0.443	0.344	0.813	0.080

Table 3
Selected bond lengths (Å) (e.s.d.s in parentheses)

Bond	Y13	Y14	Y63
C1–C1′	1.489(5)	1.489(3)	1.493(6)
C3–CL1	1.738(3)	1.738(2)	1.737(4)
C4–N1	1.392(3)	1.397(3)	1.399(5)
N1–H1	0.88(3)	0.84(2)	0.85(4)
N1–N2	1.321(3)	1.314(2)	1.308(5)
N2–C7	1.305(3)	1.309(2)	1.313(5)
C7–C8	1.481(4)	1.485(3)	1.491(6)
C8–O1	1.221(4)	1.219(3)	1.217(6)
C8–C9	1.505(4)	1.496(4)	1.492(7)
C7–C10	1.495(4)	1.492(2)	1.484(6)
C10–O2	1.228(3)	1.233(2)	1.223(5)
C10–N3	1.350(3)	1.348(3)	1.361(6)
N3–H3	0.90(3)	0.91(2)	0.86(5)
N3–C11	1.413(3)	1.413(2)	1.401(6)

Table 4
Selected bond angles (°) (e.s.d.s in parentheses)

Angle	Y13	Y14	Y63
C1′–C1–C2	121.7(2)	120.8(2)	121.4(4)
C1′–C1–C6	121.2(3)	122.1(2)	121.7(4)
C4–N1–H1	124(2)	123(2)	123(3)
C4–N1–N2	117.9(2)	118.7(2)	118.4(4)
H1–N1–N2	118(2)	119(2)	119(3)
N1–N2–C7	121.6(2)	121.4(2)	121.8(4)
N2–C7–C8	112.2(2)	112.9(2)	112.7(4)
C7–C8–O1	121.5(2)	121.5(2)	121.2(4)
C7–C8–C9	118.4(2)	118.2(2)	118.4(4)
O1–C8–C9	120.1(3)	120.3(2)	120.4(4)
N2–C7–C10	123.3(2)	123.1(2)	123.1(4)
C7–C10–O2	120.6(2)	120.3(2)	120.4(4)
O2–C10–N3	124.3(2)	124.1(2)	124.0(4)
C7–C10–N3	115.1(2)	115.6(1)	115.6(4)
C10–N3–H3	113(2)	110(1)	111(3)
C10–N3–C11	129.4(2)	129.1(2)	127.9(4)
H3–N3–C11	118(2)	120(1)	121(3)

angle is 9.0°, arising almost entirely from successive small rotations (of 2–3°) at the C4–N1, C7–N10 and C10–N3 bonds. With Y14 and Y63, the overall dihedral angle is smaller (7.5 and 6.6° respectively), reflecting slightly smaller bond rotations. In the crystallographically unsymmetrical Y12, the equivalent dihedral angles are 2° in one half of the molecule and 26° in the other. Although the molecules of Y13, Y14 and Y63 are therefore non-planar, the deviations from planarity are much less than is the case with Y12.

Table 5
Selected torsion angles (°) (e.s.d.s in parentheses)

Angle	Y13	Y14	Y63
C3–C4–N1–N2	−177.4(2)	−177.6(2)	−178.0(4)
N1–N2–C7–C10	1.1(4)	0.6(3)	1.3(6)
C7–C10–N3–C11	−177.0(2)	−176.6(2)	−177.0(4)
C4–N1–N2–C7	179.4(2)	179.5(2)	179.2(3)
N2–C7–C10–N3	−177.9(2)	−178.4(2)	−177.5(4)
C10–N3–C11–C12	180.0(3)	179.6(2)	179.0(4)

Table 6
UV–visible spectral data for solutions in dimethylformamide

Compound	λ_{max} (nm)	$\varepsilon \times 10^{-4}$ l mol^{-1} cm^{-1}
1a. Y12	431	6.63
1b. Y13	434	6.65
1c. Y14	431	7.36
1f. Y63	431	8.32
2. Y1[13]	417	1.96

The UV–visible spectral properties for solutions of the various mono and disazo pigments are given in Table 6. We have reported previously that PPP-MO calculations, assuming molecular planarity in each case, give a good account of the influence of molecular structure on colour in these series of pigments [5,13]. There is good agreement between calculated and experimental λ_{max} values and a reasonable qualitative correlation between experimental molar extinction coefficients and calculated oscillator strengths, for example explaining the significantly higher extinction coefficients of the disazo compounds compared with their monoazo analogues.The four disazo pigments show similar solution spectral characteristics, with Y13 being marginally (3nm) bathochromic compared with the other three. Y12, Y14 and Y63 in the solid state all provide somewhat greener shades than Y13 in application, while Y12 provides significantly lower colour strength than the others. It is likely that the significantly greater deviation from planarity of Y12 molecules in its crystal structure compared with the others is a determining factor explaining the lower colour strength derived from this pigment. Consistent with this is the prediction, using PPP-MO calculations modified to take account of bond rotation, that rotation about the biphenyl link in

Table 7
Intramolecular contact distances (Å) to hydrogen atoms

Compound	O2...H1	O1...H3	(nitro)O...H1	CL...H1	CL...H3
Y12[a]	1.89, 1.84	1.74, 1.95		2.45, 2.46	
Y13	1.89	1.86		2.62	
Y14	1.91	1.83		2.61	
Y63	1.92	1.88		2.62	2.51
Y1	1.84	1.78	1.91		

[a] Y12 is crystallographically non-symmetrical; the first distance given is for the essentially planar half of the molecule and the second for the twisted half [10].

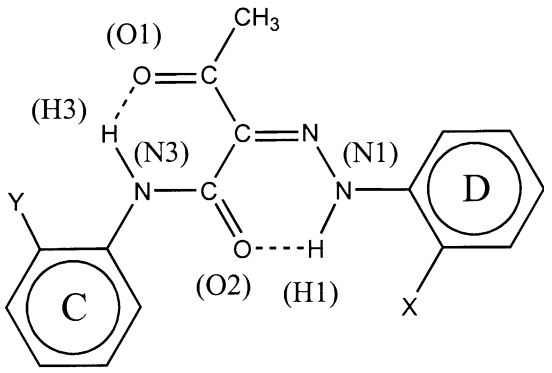

Fig. 2. Intramolecular hydrogen-bonding in azoacetoacetanilide pigments.

Y12 is likely to cause a hypsochromic shift and a reduction in intensity of the visible absorption band [5].

Hydrogen-bonding (both *intra*molecular and *inter*molecular) is commonly encountered as an important structural feature of most organic pigment classes and is observed to enhance lightfastness. It is proposed that hydrogen-bonding provides electronic and steric protection of the chromophore towards photochemical degradation, and reduces the lifetimes of photochemically excited states. Little is known about the detail of the mechanisms involved in the photofading of azo pigments. However, in the Hansa and Diarylide Yellow pigments, it is generally observed that lightfastness is enhanced by electron withdrawing substituents in the diazo component (hydrazone) ring (D in Fig. 2) [3,4]. This is consistent with the observation that certain hydrazone dyes fade by a photooxidation process initiated by attack of singlet oxygen, a process which would be inhibited by a reduction in electron density at the chromophore [14,15]. The good lightfastness of Y1 is thus associated with the strongly electron-withdrawing nitro group in the *ortho* position of hydrazone ring and the bifurcated *intra*molecular hydrogen-bonding in 6-membered rings in an essentially planar molecule. The interatomic distances given in Table 7 suggest similar, but weaker, *intra*-molecular hydrogen bonding in the Diarylides. The presence in the Diarylides of *ortho*-chlorine atoms, which are less strongly electron-withdrawing than the nitro group and where the rather long CL...H distances (ca 2.6 Å) and the narrow C–CL...H angles (ca 70°) suggests that *intra*molecular hydrogen bonds may be absent or only very weak, is probably a determining factor in the lower lightfastness of these pigments. It is also generally observed that lightfastness is enhanced by electron-releasing substituents in the coupling component (anilide) ring (C in Fig. 2), although no explanation has been given for this [3,4]. In keeping with this principle, it is generally accepted that the order of lightfastness is Y13 (two electron-releasing methyl substituents) > Y14 (one methyl) > Y63 (one chloro substituent). The electron-withdrawing electronic effect of the chlorine in the anilide ring of Y63 thus apparently overrides any compensating stabilisation effect due to the very weak intramolecular hydrogen bonding indicated by the (H3...CL2) distance (2.51 Å). It is of interest that with Y12 the intramolecular hydrogen bonding involving H3 (amide) to O2 (ketone carbonyl) is shorter in the essentially planar half of the molecule than in the twisted half. It is conceivable that this disruption of the hydrogen bonding system because of deviation from planarity

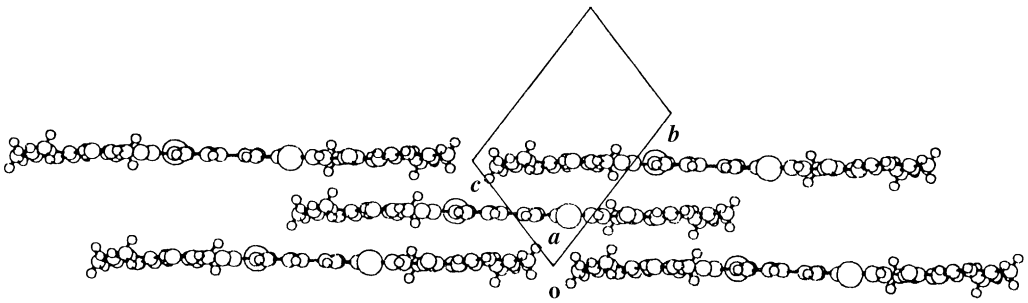

Fig. 3. Partial packing diagram for Y13 as viewed down the *a* axis. The reference molecule is in the centre; other molecules (not shown) pack head-to-tail to the left and right of the reference molecule, as in the layers above and below. The molecules above and below the reference molecule are related by non-equivalent pairs of inversion centres which are located midway between the molecules. For instance, the inversion centres at 0, $\frac{1}{2}$, 0 and 0, $\frac{1}{2}$, $-\frac{1}{2}$ are above and below the unique (right hand) half of the reference molecule. The packing of molecules in the crystals of Y14 and Y63 is of exactly the same type.

is a source of instability which accounts for the relatively poor lightfastness of Y12.

Solvent resistance in organic pigments is related to the efficiency of the molecular packing in crystals and to the strength of the intermolecular forces. The poor resistance of the monazo (Hansa) yellow pigments, such as Y1, to organic solvents may be accounted for by the observation that the molecules are small and the intermolecular interactions in the crystal structure involve only van der Waals' forces. In a few monoazo derivatives, some very weak *inter*molecular hydrogen bonding is observed which provides a slight improvement in solvent resistance [6]. There are, however, no distances between molecules in the crystal structures of Y13, Y14 and Y63 that are less than the sum of the relevant van der Waals radii, indicating that there is no *inter*molecular hydrogen bonding and thus the intermolecular interactions involve only van der Waals' forces. The improvement in solvent resistance compared with the monazo analogues is due to the overall increase in strength of the interactions between molecules as a result of their much larger molecular size.

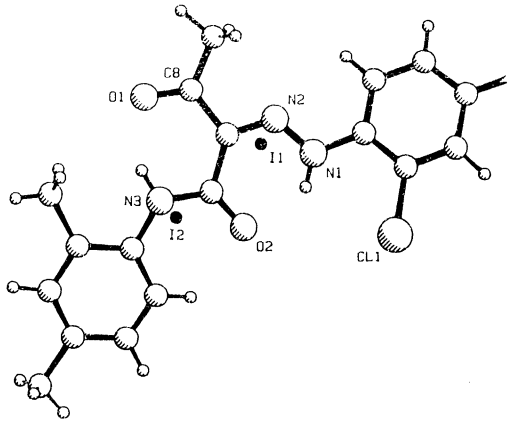

Fig. 4. View of the unique half molecule of Y13 to show the projections of the inversion centres I1 (at 0, $\frac{1}{2}$, 0) and I2 (at 0, $\frac{1}{2}$, $-\frac{1}{2}$) on to the molecular plane (defined by N1, N3 and C8). I1 therefore represents the centre of overlap with the molecule above, which is antiparallel, with N2 atoms almost above and below one another. I2 is the centre of overlap with the molecule below, which is also antiparallel, with N3 atoms almost above and below one another. The arrangements in the crystals of Y14 and Y63 are of exactly the same type.

Table 8
Some intermolecular distances and molecular volumes for Diarylide Yellow pigments

Pigment	Face to face distance (Å) to molecule above	Face to face distance (Å) to molecule below	Molecular volume[a] (Å^3)
1a, Y12[b]	3.43, 3.51	3.44, 3.47	739.2
1b, Y13	3.36	3.23	823.5
1c, Y14	3.43	3.33	771.0
1f, Y63	3.43	3.36	757.0

[a] In this case, molecular volume = unit cell volume/number of molecules per unit cell.

[b] Y12 is crystallographically non-symmetrical; the first distance given is for the essentially planar half of the molecule and the second for the twisted half [10].

The molecules of pigments Y13, Y14 and Y63 pack together in the crystal in a similar way to form an inclined, interleaved stacking arrangement, as shown for Y13 in Fig. 3, in which the angle of inclination of the molecular plane relative to the stacking axis is respectively 47.8, 45.5 or 47.7°. The molecules above and below the unique molecule are related by centres of symmetry, such that each half of each molecule is anti-parallel to those immediately above and below. However, the centres of symmetry that are above and below are not equivalent so that when viewed in projection on to the molecular plane, one of the centres of symmetry lies almost above N2 while the other lies almost below N3 (as shown in Fig. 4 for Y13). The simple interleaved stacking arrangement in these three pigments contrasts with the 'herring-bone' arrangement of interleaved stacks in the crystal structure of Yellow 12 [10].

Since the molecules are not internally planar, the perpendicular distances between molecules above and below have, for convenience, been specified in terms of the plane defined only by N1, N3 and C8. The perpendicular distances in one half of the molecule from this plane to the equivalent plane in the molecule immediately above and the corresponding distance to the equivalent plane in the molecule below are given in Table 8. This situation is repeated, in inverted form, at the other end of the molecule (for perpendicular distances between the planes defined by N1′, N3′ and C8′). The distances illustrate that molecules of Y13 pack slightly closer than Y14, even though Y13 has an extra methyl group. The difference in molecular volumes between Y12 and Y14 (Table 8) can be accounted for more or less by the volume of the additional methyl group in Y14, which indicates that there is no significant difference in overall packing efficiency between an interleaved herring-bone arrangement (Y12) and the simple stacked interleaved array (Y14). However, the molecular volume of Y13 is larger than would be expected from the presence of one additional methyl group, and this may be attributed to less efficient end to end packing caused by the *para*-methyl groups. A comparison of the intermolecular face to face distances, however, shows that in this sense Y13 packs more efficiently than Y12, and this is probably a determining factor in explaining the superior solvent resistance of Y13.

Preliminary reports have appeared of an investigation to determine the crystal structures of Y13 and 14 from powder diffraction data. The method involved indexation of the powder diagram and a combination of molecular and lattice energy calculations, using an energy minimisation approach, followed by Rietveld refinement of the most likely structures using high-quality powder diffraction profiles measured with synchrotron X-radiation [16,17]. No atomic coordinates are reported in the powder diffraction study but the space groups and molecular packing diagrams appear reasonably consistent with the results reported here from single crystal analysis. The powder study indicates that Y13 and Y14 have similar crystal structures which may be indexed with a triclinic lattice, although the choice of unit cells is different from ours. The choice of cell axes in the triclinic system is arbitrary (there are no symmetry axes or planes) and our choices were for practical convenience for two-circle diffractometry. However, the cell volumes should be the same for alternative triclinic (P) lattices. The volumes obtained from the single crystal data and those calculated from the cell parameters of the powder studies show close agreement [Y13: 823.5 $Å^3$ (single crystal) compared with 826.6 $Å^3$ (powder); Y14: 771.0 $Å^3$ (single crystal) compared with 772.3 $Å^3$ (powder)]. The determinations from powder diffraction suggest centrosymmetric molecules with a planar biphenyl fragment and with the outer anilide rings twisted by 4–10°, consistent with the results of the single crystal determination.

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