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The crystal structure of C.I. Pigment Yellow 12

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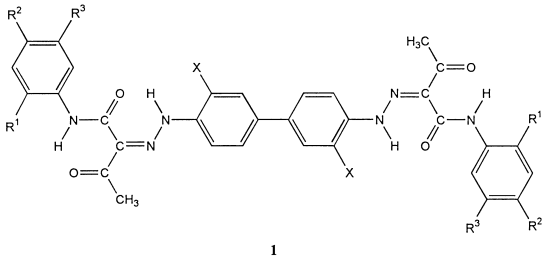
Abstract

The X-ray crystal structure of C.I. Pigment Yellow 12, 2,2′-[(3,3′-dichloro[1,1′-biphenyl]-4,4′-diyl)bis(azo)bis[3-oxo-*N*-phenylbutanamide], is described. This is the first reported single crystal determination for a disazoacetoacetanilide (Diarylide Yellow) pigment. The molecules exist in the bisketohydrazone form which is structurally analogous to the hydrazone form adopted by the monoazoacetoacetanilide (Hansa Yellow) pigments. Notable features of crystalline C.I. Pigment Yellow 12 are that the molecules are not constrained by crystallographic symmetry and that they are not planar. Some intramolecular hydrogen bonding is observed, but there is no intermolecular hydrogen bonding.

Keywords: X-ray crystallography; C.I. Pigment Yellow 12; Disazoacetoacetanilide; Diarylide Yellow; Disazo pigment; Ketohydrazone

1. Introduction



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The most important of the yellow classical organic pigments are a series of disazoacetoacetanilides, commonly referred to as Diarylide Yellows [1–3]. These pigments are characterised by their ability to provide intense, bright colours and high transparency at relatively low cost. They are commonly the yellow pigments of choice for the coloration of printing inks, and they also find some use in paints and plastics. Although these compounds are 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 [4]. The chemical structures of the most important commercial products in the series are shown in Table 1. These pigments are invariably symmetrically-substituted compounds, and are synthesised by an azo coupling reaction of a tetrazotised benzidine derivative, most commonly 3,3′-dichlorobenzidine (1 mol) with an acetoacetanilide coupling component (2 mol). C.I. Pigment Yellow 12 (**1a**) is one of the most important commercial products of this series, and is the simplest of these compounds

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Table 1
The substituent pattern in industrially important disazoaceto-acetanilide pigments

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

in that there are no substituents on the aceto-acetanilide phenyl rings.

Pigments are finely-divided crystalline colouring materials which are incorporated by a dispersion process into their application media, in which they are required to be insoluble. They are retained in their application as discrete solid particles fixed within a polymeric matrix. As a result, the optical properties of pigments (including colour and transparency) and their fastness properties (for example to light, heat and solvents) are dependent on their molecular structure and also on their solid phase characteristics (including particle size and shape distribution and the crystallographic arrangement). X-ray single crystal structural studies on pigments are capable of providing details of the crystallographic arrangement including details of the intramolecular and intermolecular interactions within the crystal structure and this information assists towards understanding the technical performance of the products. In view of the commercial importance of the disazoaceto-acetanilides, it is somewhat surprising that no single crystal structure determinations have been previously reported in the literature, although the results of structural studies on C.I. Pigments Yellow 13 (**1b**) and 14 (**1c**) using X-ray powder diffraction methods were presented at a recent conference [5,6]. The absence of single crystal structural data may be due in part to the extreme insolubility of these compounds which makes growing single crystals suitable for X-ray analysis extremely difficult. These disazo pigments are structurally analogous to the Hansa Yellows, a series of monoazoacetoacet-anilide pigments. The crystal structures of a number of these monoazo pigments have appeared in the literature [7–19], and the results have been reviewed [20]. In this paper, we report the X-ray single crystal structure of C.I. Pigment Yellow 12 (**1a**).

Table 2
Fractional atomic co-ordinates and equivalent isotropic displacement parameters ($Å^2$) for C.I. Pigment Yellow 12 (**1a**)

Atom	x/a	y/b	z/c	U_{eq}[a]
CL1	0.32965(10)	0.2480(3)	0.01510(8)	0.0510(12)
N1	0.4821(3)	0.2428(10)	−0.0044(2)	0.038(4)
N2	0.5458(3)	0.2341(8)	−0.0199(2)	0.033(3)
N3	0.4611(4)	0.0742(8)	−0.1731(2)	0.038(4)
O1	0.6200(3)	0.1263(8)	−0.1321(2)	0.052(3)
O2	0.3992(3)	0.1235(7)	−0.1066(2)	0.048(3)
C1	0.4968(4)	0.4186(9)	0.1664(3)	0.034(4)
C2	0.4249(4)	0.3654(10)	0.1243(3)	0.034(4)
C3	0.4217(4)	0.3100(9)	0.0686(3)	0.035(4)
C4	0.4890(4)	0.3046(9)	0.0525(3)	0.035(4)
C5	0.5610(4)	0.3628(10)	0.0935(3)	0.036(5)
C6	0.5645(4)	0.4168(10)	0.1493(3)	0.036(5)
C7	0.5396(4)	0.1767(9)	−0.0733(3)	0.031(4)
C8	0.6163(4)	0.1739(10)	−0.0840(3)	0.041(5)
C9	0.6908(6)	0.2316(19)	−0.0357(4)	0.058(7)
C10	0.4604(4)	0.1209(10)	−0.1191(3)	0.038(5)
C11	0.3946(4)	0.0214(10)	−0.2232(3)	0.035(4)
C12	0.4005(5)	0.0475(11)	−0.2782(3)	0.047(5)
C13	0.3393(6)	−0.0073(13)	−0.3295(3)	0.058(6)
C14	0.2719(6)	−0.0880(12)	−0.3260(4)	0.060(7)
C15	0.2660(5)	−0.1154(12)	−0.2700(4)	0.055(6)
C16	0.3268(4)	−0.0611(10)	−0.2191(4)	0.041(5)
CL1′	0.66963(12)	0.4875(4)	0.39030(8)	0.0594(14)
N1′	0.5207(4)	0.6387(9)	0.3996(2)	0.040(4)
N2′	0.4578(3)	0.7034(8)	0.4090(2)	0.039(4)
N3′	0.5287(3)	0.7872(9)	0.5679(2)	0.042(4)
O1′	0.3782(3)	0.8766(9)	0.5106(2)	0.060(4)
O2′	0.5964(3)	0.6610(7)	0.5126(2)	0.049(3)
C1′	0.5037(4)	0.4790(10)	0.2273(3)	0.034(4)
C2′	0.5728(5)	0.4556(10)	0.2749(3)	0.038(5)
C3′	0.5786(4)	0.5123(10)	0.3312(3)	0.040(4)
C4′	0.5130(4)	0.5876(10)	0.3416(3)	0.037(5)
C5′	0.4442(5)	0.6083(11)	0.2943(3)	0.044(5)
C6′	0.4380(4)	0.5545(11)	0.2381(3)	0.040(5)
C7′	0.4615(4)	0.7490(10)	0.4630(3)	0.039(4)
C8′	0.3842(4)	0.8186(11)	0.4644(3)	0.051(5)
C9′	0.3126(5)	0.8160(17)	0.4080(4)	0.057(6)
C10′	0.5345(4)	0.7280(11)	0.5167(3)	0.044(5)
C11′	0.5882(4)	0.7905(10)	0.6255(3)	0.041(5)
C12′	0.5660(5)	0.8656(12)	0.6705(3)	0.051(6)
C13′	0.6198(6)	0.8795(13)	0.7285(4)	0.063(6)
C14′	0.6956(6)	0.8128(14)	0.7403(4)	0.065(7)
C15′	0.7192(5)	0.7370(13)	0.6963(4)	0.057(6)
C16′	0.6658(5)	0.7244(12)	0.6389(4)	0.055(6)

[a] $U_{eq} = (1/3)\Sigma\Sigma U_{ij} a_i^* . a_j^* . a_i . a_j .$

2. Experimental

2.1. Synthesis and crystallisation

C.I. Pigment Yellow 12 (**1a**) was prepared by tetrazotisation of 3,3′-dichlorobenzidine, followed by azo coupling of the resulting tetrazonium salt with acetoacetanilide using well-established procedures [4]. Crystals suitable for X-ray analysis were grown from solutions in 1,2,4-trichlorobenzene by slow cooling from 200°C over a period of several days.

2.2. Crystal structure determination

2.2.1. Crystal data

$C_{32}H_{26}Cl_2N_6O_4$	Mo K_α radiation
$M_r = 629.5$	$\lambda = 0.7107$ Å
Monoclinic	Cell parameters from 16 reflections
$P\ 1\ 2_1\ /n\ 1$	$\theta = 6$–$11°$
$a = 17.850(6)$ Å	$\mu = 0.26$ mm^{-1}
$b = 7.37(1)$ Å	$T = 293$ K
$c = 24.005(8)$ Å	Lozenges
$\beta = 110.57(3)°$	$0.40 \times 0.32 \times 0.16$ mm
$V = 2956.6$ Å^3	Orange
$Z = 4$	
$D_x = 1.41$ Mg m^{-3}	
D_m not measured	

Table 3
Fractional atomic co-ordinates and isotropic displacement parameters (Å^2) for hydrogen atoms

Atom	x/a	y/b	z/c	U
H1	0.432(4)	0.217(9)	−0.031(3)	0.05(2)
H2	0.374(3)	0.348(7)	0.134(2)	0.02(1)
H3	0.508(3)	0.074(8)	−0.178(2)	0.02(2)
H5	0.609(4)	0.365(9)	0.082(3)	0.06(2)
H6	0.612(3)	0.475(8)	0.174(2)	0.03(2)
H12	0.447(3)	0.105(7)	−0.279(2)	0.02(2)
H13	0.351(4)	0.030(10)	−0.365(3)	0.06(2)
H14	0.222(5)	−0.123(13)	−0.365(4)	0.13(4)
H15	0.218(5)	−0.171(12)	−0.266(3)	0.09(3)
H16	0.323(3)	−0.076(8)	−0.180(3)	0.04(2)
H91	0.693(5)	0.338(11)	−0.025(4)	0.07(3)
H92	0.690(4)	0.202(12)	0.004(3)	0.09(3)
H93	0.738(5)	0.182(13)	−0.042(4)	0.12(4)
H1′	0.573(5)	0.620(11)	0.431(3)	0.09(3)
H2′	0.619(3)	0.416(8)	0.274(2)	0.02(2)
H3′	0.471(5)	0.831(11)	0.563(3)	0.09(3)
H5′	0.398(3)	0.651(8)	0.299(2)	0.04(2)
H6′	0.392(3)	0.574(7)	0.206(2)	0.02(2)
H12′	0.516(3)	0.905(7)	0.660(2)	0.02(2)
H13′	0.597(5)	0.939(12)	0.758(4)	0.11(3)
H14′	0.734(5)	0.827(11)	0.774(3)	0.08(3)
H15′	0.775(4)	0.690(9)	0.708(3)	0.05(2)
H16′	0.676(5)	0.665(12)	0.609(4)	0.11(4)
H91′	0.289(4)	0.689(10)	0.406(3)	0.04(2)
H92′	0.321(5)	0.855(13)	0.373(4)	0.12(4)
H93′	0.275(5)	0.914(12)	0.409(4)	0.10(3)

2.2.2. Data collection

Stoe Stadi-2 2 circle diffractometer	1723 observed reflections $[F_o > 4\sigma(F_o)]$
ω-step scans	$\theta_{max} = 25°$
No adsorption correction	$h = 0 \rightarrow 19$
5540 measured reflections	$k = 0 \rightarrow 8$
4943 independent reflections	$1 = -26 \rightarrow +25$
	2 standard reflections for each layer; frequency 60 min
	Intensity variation: ±3%

2.2.3. Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.09$
$R = 0.048$	$\Delta\rho_{max} = 0.25$ e Å^{-3}
$wR = 0.048$	$\Delta\rho_{min} = -0.22$ e Å^{-3}
1723 reflections	Extinction correction: isotropic
502 parameters	$F'_c = F_c\left(1 - gF_c^2/\sin\theta\right)$, where $g = 4.5(12) \times 10^{-8}$
All H-atom parameters refined	Atomic scattering factors from SHELX76 [21]

The space group and approximate cell parameters were obtained from oscillation and Weisenberg photographs (Cu K_α radiation). Final values for the cell parameters a, c and β were obtained from ω and 2θ angles for 16 $h0l$ reflections, and b was determined from ± μ scans for two $0k0$ reflections. Intensity data (Mo K_α, graphite monochromator) were corrected for Lorentz and polarisation effects using SHELX76 [21]. All non-H atoms were located

by direct methods using SHELXS86 [22]. All H atoms were located from difference Fourier syntheses. The structural parameters were refined by least squares calculations using two overlapping large block matrices in alternate cycles. The final least squares weighting scheme was

$w = 1/\left[1 + 0.004(40 - F_o)^2\right]$ for $F_o < 40$, and

$w = 1/\left[1 + 0.005(F_o - 40)^2\right]$ for $F_o > 40$.

Atomic parameters and derived geometrical quantities are given in Tables 2–7.

Table 4
Anisotropic displacement parameters for non-hydrogen atoms

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
CL1	0.0376(10)	0.0823(16)	0.0458(10)	−0.0210(12)	0.0108(8)	−0.0088(13)
N1	0.030(3)	0.055(40)	0.033(3)	0.003(4)	0.009(3)	−0.002(4)
N2	0.041(3)	0.030(4)	0.036(3)	0.002(3)	0.020(3)	−0.005(3)
N3	0.037(4)	0.049(5)	0.040(4)	−0.009(3)	0.020(3)	0.007(3)
O1	0.049(3)	0.083(4)	0.042(3)	−0.011(3)	0.023(2)	−0.004(3)
O2	0.041(3)	0.081(4)	0.043(3)	−0.019(3)	0.021(2)	−0.005(3)
C1	0.031(4)	0.039(5)	0.033(4)	0.001(3)	0.013(3)	0.000(3)
C2	0.029(4)	0.046(5)	0.032(4)	0.004(4)	0.013(3)	0.001(4)
C3	0.032(4)	0.038(5)	0.036(4)	−0.005(4)	0.009(3)	0.004(4)
C4	0.051(5)	0.032(5)	0.025(4)	−0.001(3)	0.013(3)	0.000(4)
C5	0.030(4)	0.055(6)	0.029(4)	−0.007(4)	0.009(3)	−0.005(4)
C6	0.036(4)	0.041(5)	0.034(4)	−0.008(4)	0.002(4)	−0.013(4)
C7	0.033(4)	0.031(5)	0.034(4)	0.002(3)	0.017(3)	0.000(3)
C8	0.037(4)	0.052(6)	0.039(4)	−0.004(4)	0.014(3)	−0.003(4)
C9	0.053(6)	0.076(9)	0.061(6)	−0.020(7)	0.026(5)	−0.003(6)
C10	0.044(5)	0.037(5)	0.041(4)	0.002(4)	0.023(4)	0.006(4)
C11	0.040(4)	0.032(5)	0.029(4)	−0.004(4)	0.001(3)	0.000(4)
C12	0.042(5)	0.054(6)	0.045(5)	−0.007(4)	0.015(4)	0.001(5)
C13	0.068(6)	0.066(7)	0.040(5)	−0.006(5)	0.005(5)	0.000(6)
C14	0.059(6)	0.049(6)	0.076(7)	−0.013(6)	−0.004(6)	0.017(5)
C15	0.041(5)	0.046(6)	0.078(7)	0.000(5)	0.006(5)	0.007(5)
C16	0.040(5)	0.031(5)	0.052(5)	−0.003(4)	0.013(4)	0.002(4)
CL1′	0.0575(12)	0.1032(19)	0.0399(10)	−0.0171(13)	−0.0036(9)	0.0312(14)
N1′	0.046(4)	0.052(4)	0.034(4)	−0.006(3)	0.021(3)	0.004(4)
N2′	0.054(4)	0.042(4)	0.036(3)	−0.004(3)	0.027(3)	−0.002(3)
N3′	0.044(4)	0.069(5)	0.028(3)	−0.010(3)	0.015(3)	0.003(4)
O1′	0.059(4)	0.120(5)	0.043(3)	−0.018(3)	0.026(3)	0.014(3)
O2′	0.047(3)	0.085(5)	0.033(3)	−0.007(3)	0.014(2)	0.013(3)
C1′	0.036(4)	0.037(5)	0.027(4)	0.002(4)	0.006(3)	0.006(4)
C2′	0.039(5)	0.044(5)	0.036(4)	−0.011(4)	0.010(4)	0.010(4)
C3′	0.043(4)	0.040(5)	0.033(4)	−0.003(4)	0.001(3)	0.001(4)
C4′	0.046(4)	0.037(5)	0.034(4)	−0.002(4)	0.014(4)	0.012(4)
C5′	0.039(5)	0.058(6)	0.039(5)	−0.003(4)	0.013(4)	0.004(4)
C6′	0.035(4)	0.055(6)	0.032(4)	0.007(4)	0.007(4)	0.005(4)
C7′	0.050(4)	0.035(5)	0.040(4)	0.005(4)	0.021(3)	0.002(4)
C8′	0.044(5)	0.078(7)	0.037(4)	0.001(4)	0.012(4)	−0.003(5)
C9′	0.044(5)	0.073(8)	0.055(6)	0.001(6)	0.014(4)	0.002(6)
C10′	0.042(4)	0.055(6)	0.044(4)	−0.004(4)	0.021(3)	0.002(5)
C11′	0.053(5)	0.040(5)	0.035(4)	−0.007(4)	0.016(4)	0.000(4)
C12′	0.051(5)	0.059(6)	0.045(5)	−0.008(5)	0.016(4)	0.008(5)
C13′	0.077(7)	0.066(7)	0.048(5)	−0.004(5)	0.020(5)	−0.001(6)
C14′	0.077(7)	0.069(8)	0.047(6)	−0.004(5)	−0.005(6)	−0.011(6)
C15′	0.045(5)	0.067(7)	0.055(5)	0.004(6)	−0.002(4)	0.002(5)
C16′	0.052(5)	0.052(6)	0.057(6)	0.002(5)	0.012(4)	0.007(5)

3. Results and discussion

The crystallographic asymmetric unit is a single complete molecule, and all molecules are equivalent. The crystal structure confirms that the molecule exists in the bisketohydrazone form. The molecular geometry is not constrained by crystallographic symmetry and the molecule is not planar as may be observed by inspection of Fig. 1. The observed conformation may be more or less completely generated from a hypothetical planar molecule by applying only two operations: firstly, a torsional rotation of 27° around the central C1–C1′ bond (the biphenyl link) and secondly, another torsional rotation of 26°, in the same sense, around the CL1–N3 bond (the terminal phenyl to amide link). This results in one half of the molecule (C1′–C16′) being essentially planar, while the other half is twisted relative to this plane and is also internally twisted. Dihedral angles between relevant planes within the molecule are given in Table 7. It is likely that the non-planarity of C.I. Pigment Yellow 12 molecules in its crystal structure will have an influence on its colour properties. It has been suggested previously, as a

Table 5
Selected intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses

C1– C1′ 1.490(8)			
C3–CL1	1.753(6)	C3′–CL1′	1.751(7)
C4–N1	1.402(8)	C4′–N1′	1.402(9)
N1–N2	1.318(7)	N1′–N2′	1.311(8)
N1–H1	0.92(6)	N1′–H1′	0.98(8)
N2–C7	1.316(8)	N2′–C7′	1.318(8)
C7–C8	1.481(9)	C7′–C8′	1.483(10)
C8–O1	1.230(8)	C8′–O1′	1.227(9)
C8–C9	1.486(12)	C8′–C9′	1.500(11)
C7–C10	1.510(9)	C7′–C10′	1.485(9)
C10–O2	1.231(8)	C10′–O2′	1.245(8)
C10–N3	1.347(8)	C10′–N3′	1.343(9)
N3–C11	1.415(8)	N3′–C11′	1.418(8)
N3–H3	0.89(5)	N3′–H3′	1.04(8)
H1...CL1	2.45(5)	H1′...CL1′	2.46(7)
H1...O2	1.84(6)	H1′...O2′	1.89(8)
H3...O1	1.95(5)	H3′...O1′	1.74(7)
C1′–C1–C2	122.5(6)	C1–C1′–C2′	1.213(6)
C1′–C1–C6	120.3(5)	C1–C1′–C6′	120.8(6)
C2–C3–CL1	119.7(5)	C2′–C3′–CL1′	119.4(5)
C4–C3–CL1	118.0(5)	C4′–C3′–CL1′	119.5(5)
C3–C4–N1	119.4(6)	C3′–C4′–N1′	119.4(6)
C5–C4–N1	122.5(6)	C5′–C4′–N1′	123.0(6)
C4–N1–N2	120.1(5)	C4′–N1′–N2′	118.5(6)
C4–N1–H1	118(4)	C4′–N1′–H1′	117(5)
N1–N2–C7	120.4(5)	N1′–N2′–C7′	120.8(5)
N2–C7–C8	114.0(5)	N2′–C7′–C8′	112.7(6)
N2–C7– C10	122.2(5)	N2′–C7′–C10′	123.5(6)
C8–C7–C10	123.8(5)	C8′–C7′–C10′	123.8(6)
C7–C8–O1	121.6(6)	C7′–C8′–O1′	121.2(6)
C7–C8–C9	119.3(6)	C7′–C8′–C9′	118.7(6)
O1–C8–C9	119.1(6)	O1′–C8′–C9′	120.1(7)
C7–C10–O2	120.1(6)	C7′–C10′–O2′	120.4(6)
C7–C10–N	116.6(6)	C7′–C10′–N3′	115.7(6)
O2– C10– N3	123.2(6)	O2′–C10′–N3′	123.9(6)
C10–N3–C11	126.9(6)	C10′–N3′–C11′	128.7(6)
C10–N3–H3	118(3)	C10′–N3′–H3′	113(4)
C11–N3–H3	116(3)	C11′–N3′–H3′	118(4)
N3–C11–C12	116.9(6)	N3′–C11′–C12′	116.3(6)
N3–C11–C16	123.4(6)	N3′–C11′–C16′	124.2(6)
N1–H1...CL1	111(4)	N1′–H1...CL1′	112(5)
N1–H1...O2	131(5)	N1′–H1′...O2′	125(6)
N3–H3...O1	138(4)	N3′–H3′...O1′	142(6)

Table 6
Selected torsion angles (°)

C2′–C1′–C1–C6	−30.2(10)	C2–C1–C1′–C2′	150.9(7)
C6′–C1′–C1–C2	−26.1(10)	C6–C1–C1′–C6′	152.8(7)
CL1–C3–C4–N1	−2.8(8)	CL1′–C3′–C4′–N1′	−1.3(9)
C3–C4–N1–N2	−178.9(6)	C3′–C4′–N1′–N2′	−177.7(6)
C5–C4–N1–N2	1.8(10)	C5′–C4′–N1′–N2′	2.5(10)
C4–N1–N2–C7	−179.8(6)	C4′–N1′–N2′–C7′	178.3(6)
N1–N2–C7–C8	−179.8(6)	N1′–N2′–C7′–C8′	179.8(6)
N1–N2–C7–C10	0.7(9)	N1′–N2′–C7′–C10′	−1.4(10)
N2–C7–C8–C9	0.6(10)	N2′–C7′–C8′–C9′	4.5(10)
N2–C7–C8–O1	−178.9(6)	N2′–C7′–C8′–O1′	−175.9(7)
N2–C7–C10–O2	−2.0(10)	N2′–C7′–C10′–O2′	−1.5(11)
N2–C7–C10–N3	176.4(6)	N2′–C7′–C10′–N3′	177.7(6)
C8–C7–C10–O2	178.6(6)	C8′–C7′–C10′–O2′	176.8(7)
C8–C7–C10–N3	−3.0(9)	C8′–C7′–C10′–N3′	−4.0(10)
C7–C10–N3–C11	−178.5(6)	C7′–C10′–N3′–C11′	−177.9(6)
C10–N3–C11–C12	155.3(7)	C10′–N3′–C11′–C12′	177.9(7)
C10–N3–C11–C16	−27.6(11)	C10′–N3′–C11′–C16′	−1.9(12)

Table 7
Dihedral angles (°) between planes of atoms[a]

Plane 1 and plane 1′	26.7
Plane 1 and plane 2	25.8
Plane 1′ and plane 2′	2.0
Plane 2 and plane 2′	47.8

[a] Plane 1 is defined by C1, C2, C3, C4, C5, C6; plane 2 is defined by C11, C12, C13, C14, C15, C16; plane 1′ is defined by C1′, C2′, C3′, C4′, C5′, C6′; plane 2′ is defined by C11′, C12′, C13′, C14′, C15′, C16′.

result of PPP-MO calculations modified to account for the influence of bond rotation, that rotation about the biphenyl link in C.I. Pigment Yellow 12 is likely to cause a hypsochromic shift and reduction in intensity of the visible absorption band in solution [4].

Each half of the molecule exists in a ketohydrazone form which is structurally similar to the closely-related monoazoacetacetanilide (Hansa Yellow) pigments [7–20]. Important bond lengths which may be highlighted in this respect are the N–N (1.319 and 1.312 Å), the hydrazone C–N (1.317 and 1.319 Å) and the ketone C–O (1.231 and 1.228 Å), which in each case are comparable with the bond lengths reported for the monoazo analogues. Within each half of the C.I. Pigment Yellow 12 molecule there are H1...CL1, H1...O2 and H3...O1 contacts which are short enough for some degree of hydrogen bonding interaction (see Table 4). Similar bifurcated *intra*molecular hydrogen bonding is observed in the monoazoacetoacetanilides, and this feature has been used to account

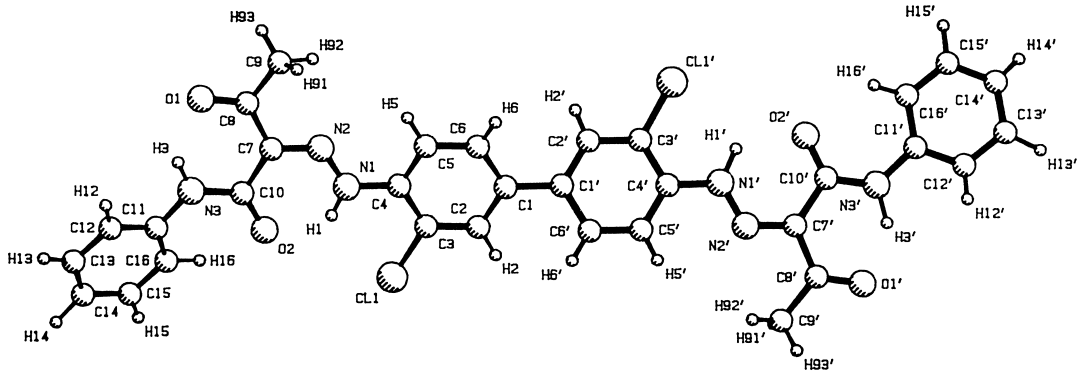

Fig. 1. View of a molecule of C.I. Pigment Yellow 12 (**1a**), showing the atomic numbering scheme.

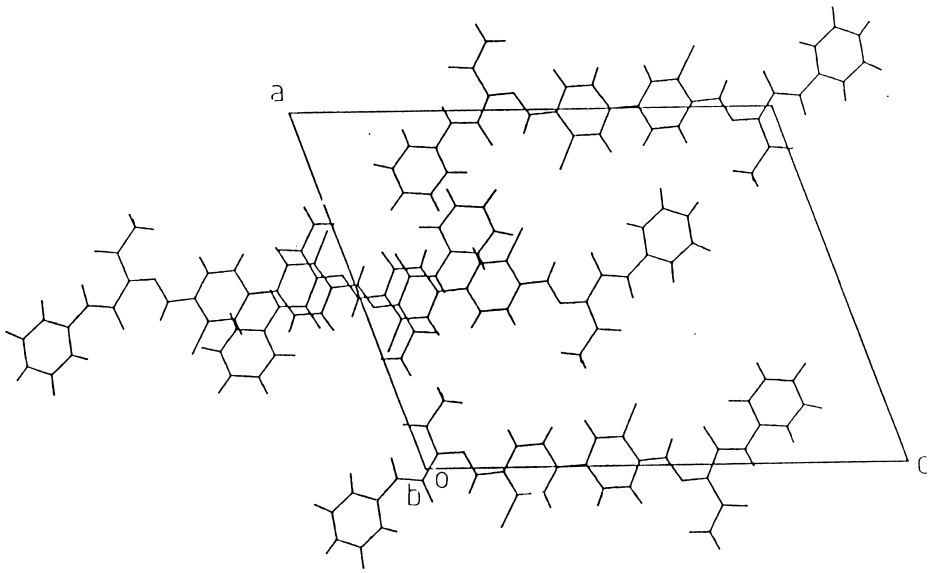

Fig. 2. View of molecules in the unit cell projected on to the *a c* plane.

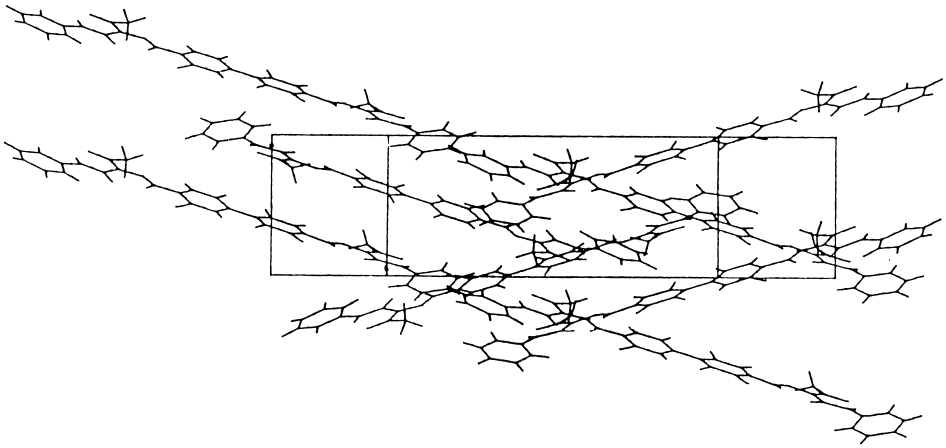

Fig. 3. View of molecules and a unit cell to show the packing of molecules into inclined stacks.

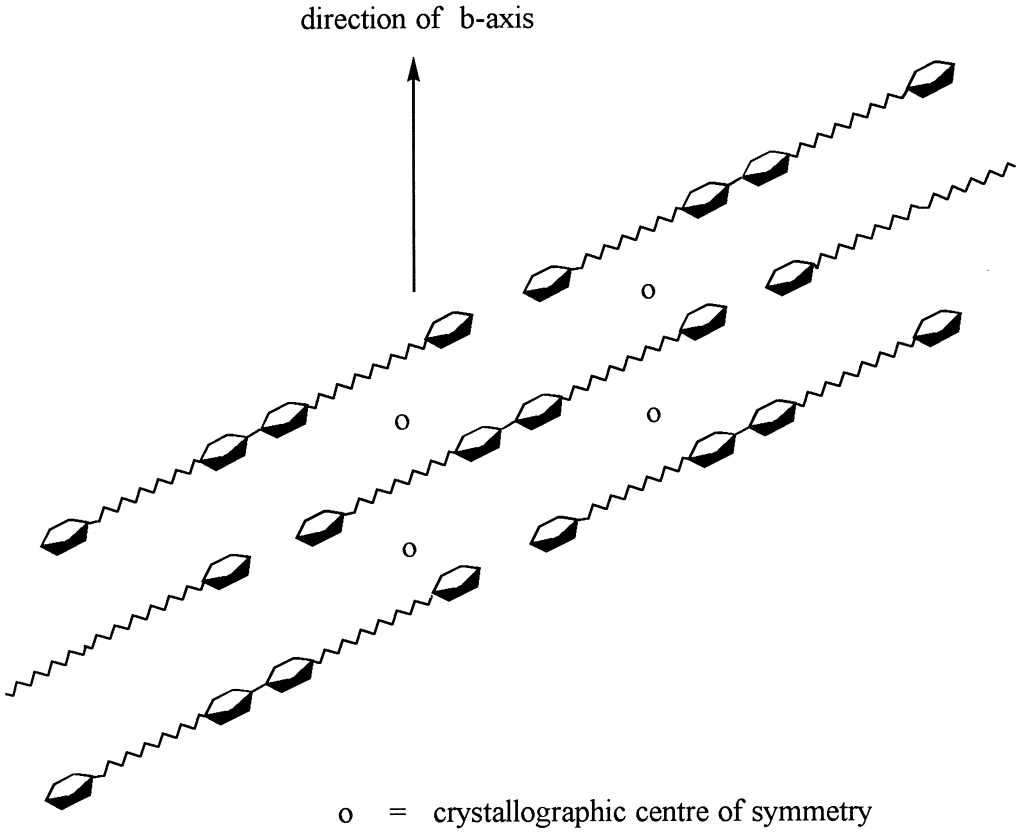

Fig. 4. Representation of interleaved molecules in the inclined stack and showing some of the crystallographic centres of symmetry.

for their relatively good lightfastness properties. There are no *inter*molecular contacts close enough for hydrogen bonding.

The crystallographic arrangement of C.I. Pigment Yellow 12 molecules is illustrated in Figs. 2 and 3. Molecules pack in the crystal lattice to form inclined stacks of interleaved molecules (Fig. 4 is a simplified representation). The plane of the ketohydrazone group of each half of each molecule lies sandwiched between the planes of the ketohydrazone groups of the molecules that are above and below, but the middle molecule is crystallographically inverted relative to those above and below. For the planar half of the molecule, the two perpendicular distances for the sandwich are: top-to-middle = 3.43 Å and middle-to-bottom = 3.44 Å. For the twisted half of the molecule the distances are respectively 3.51 and 3.47 Å.

We have also determined the crystal structures for a range of related disazo compounds including C.I. Pigments Yellow 13, 14, 63 and 83. There are several variations for molecular packing in the crystal states of these compounds and these will be compared in subsequent publications. A preliminary account of this structure determination has been reported by Lough [23].

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