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The crystal and molecular structure of C.I. Pigment Yellow 83, a superior performance Diarylide Yellow pigment

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Abstract

The pigment (Y83) crystallises in the monoclinic system, space group $P2_1/c$, with two molecules in the unit cell. The molecules exist in the bisketohydrazone tautomeric form and have crystallographic C_i symmetry. The *intra*molecular hydrogen bonding normally associated with this structural arrangement is observed, but there is no *inter*molecular hydrogen bonding. The crystal structure differs from those of previously reported Diarylide Yellow pigments (Y12, Y13, Y14 and Y63) in that the molecules are more nearly planar and the packing arrangement involves simple inclined stacks. The difference in crystal packing for Y83 is consistent with its inability to form solid solutions with the other pigments. The colour properties and technical performance of the pigment are discussed in relation to its crystal structure.

Keywords: X-ray crystallography; C.I. Pigment Yellow 83; Disazoacetoacetanilide; Diarylide Yellow; Disazo pigment; Ketohydrazone; Solid solution

1. Introduction

The Diarylide Yellows (disazoacetoacetanilides) constitute the most important group of yellow classical organic pigments [1–4]. The substituent pattern in the most important commercial products in the series of disazo pigments, which exist in the bisketohydrazone form **(1)** both in solution and in solid state phases [5], is given in Table 1. This series of pigments generally provides, at relatively low cost, bright yellow to orange colours, high colour strength, high transparency, and reasonable solvent resistance but commonly only moderate lightfastness. They are particularly suited to printing ink applications and are in fact the dominant yellow pigments used for this purpose. C.I. Pigment Yellow 83 (**1g**, Y83) owes its particular importance to its strong, bright reddish-yellow colour and its superior lightfastness and solvent resistance compared with other Diarylide Yellows, and consequently it is suited to a wider range of applications. Fine particle size grades are used in printing inks while larger particle size grades with superior opacity are suitable for use in industrial coatings. The technical performance of organic pigments is dependent not only on their molecular structure but also on their solid state characteristics, including particle size and morphology and the crystal structural arrangement.

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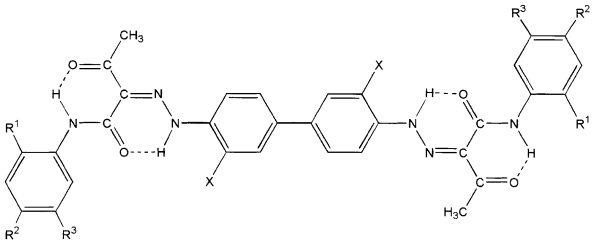

X-ray single crystal studies of pigments provide important information which assists understanding of the technical performance of the products and is an essential first stage in the crystal engineering of new products for enhanced physical and chemical properties. We have previously published the X-ray single crystal structures of four of the most important industrial Diarylide yellow pigments (**1a**, Y12), (**1b**, Y13), (**1c**, Y14) and (**1f**, Y63) [6,7] and have established relationships between the crystallographic properties of the pigments and their colouristic and technical performance. We now report the crystal structure of Y83 and discuss the reasons for its superior performance.

2. Experimental

2.1. Synthesis and crystallisation

C. I. Pigment Yellow 83, 2,2′-[(3,3′-dichloro[1,1-biphenyl]-4,4′-diyl)bis(azo)bis[*N*-(4-chloro-2,5-dimethoxyphenyl)-3-oxobutanamide] was prepared by tetrazotisation of 3,3′-dichlorobenzidine, followed by azo coupling of the resulting tetrazonium salt with *N*-(4′-chloro-2′,5′-dimethoxyphenyl)-3-oxobutanamide (AADMCA) using well-established procedures [5]. The pigment is the most insoluble of the series of disazo pigments which we have investigated and as such proved extremely difficult to crystallise. Crystals were grown for X-ray analysis from solutions of the pigment in 1,2,4-trichlorobenzene, contained in sealed tubes, by slow cooling from 200 °C over a period of several days. In total, 45 separate crystallisation experiments were performed but the crystals obtained were of rather low quality.

2.2. Crystal data

$C_{36}H_{32}Cl_4N_6O_8$, $M_r = 818.48$; yellow-orange needle (0.08 × 0.2 × 0.4mm), monoclinic; space group $P2_1/c$; $a = 5.106(9)$, $b = 20.627(3)$, $c = 17.009(15)$ Å; $\beta = 98.4(3)$ °, $V = 1772.2$ Å^3, $Z = 2$, $D_x = 1.32$ Mg m^{-3}, $D_c = 1.53$ Mg m^{-3}, $T = 295$ K; $\lambda = 0.71073$ Å (Mo K_α radiation); $\mu = 0.4$ mm^{-1}. The space group 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). Intensities were measured for 2839 reflections from the layers $0 \rightarrow 5$, k, l, giving 2501 unique reflections of which 805 had $F_o > 4\sigma(F_o)$. Intensity data were corrected for Lorentz and polarisation effects but not for absorption. Structure solution was by direct methods [8] and structure refinements by least squares [9] to minimise $\sum(|F_o|-|F_c|)^2$ with unit weights for all reflections. All hydrogen atoms were located from difference Fourier syntheses. The relatively poor quality crystal gave fewer observed reflections than would be ideal and so anisotropic vibration parameters were used only for the heaviest atoms (Cl, O and N) and for the methyl carbon atoms (C9, C17 and C18). The remaining carbon atoms and all hydrogen atoms were included in the refinement with isotropic thermal vibration parameters. A final difference Fourier synthesis showed no peaks or troughs outside the range ±0.25 e Å^{-3}; final $R = 0.050$.

3. Results and discussion

Fig. 1 shows the molecular structure of Y83, with the appropriate atomic labelling scheme. Atomic parameters and derived geometrical quantities are given in Tables 2-5. The crystal structure determination confirms that the molecule exists in the bis-ketohydrazone tautomeric form, similar to the other disazoacetoacetanilides [6,7] and their monoazo analogues (Hansa Yellows) [10].

The angles between the planes defined by the aromatic rings for the five Diarylide Yellow

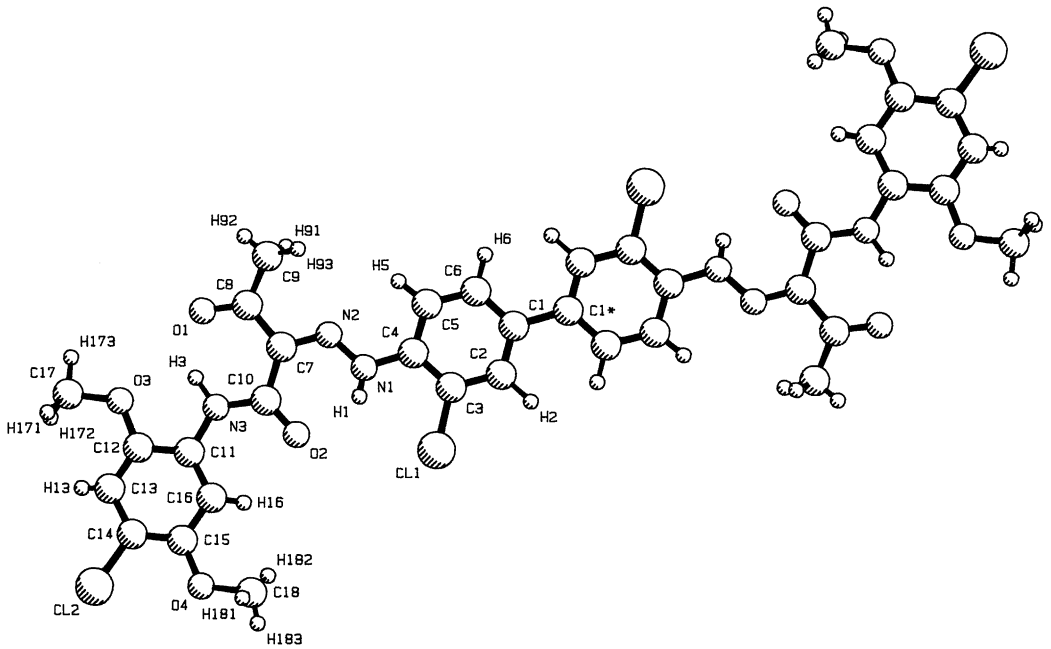

Fig. 1. Molecular structure and atomic numbering scheme for Y83.

pigments studied so far are given in Table 6 (with reference to Fig. 2). In crystalline Y83, the central and terminal aromatic rings are more nearly parallel than is the case with any of the other pigments. In Y83, as with Y13, Y14 and Y63, the molecules have a crystallographic centre of symmetry located midway between C1 and C1′ (the biphenyl linkage) which means that the two biphenyl rings must be parallel to one another. In Y83, as with Y14 and Y63, the biphenyl rings are also coplanar. The atoms C1′ to C6′ have negligible displacements from the plane defined by C1–C6 so that the biphenyl link (C1–C1′) shows no out-of plane bend. Y13 has a slightly out-of-plane biphenyl link. Molecules of Y12 have no crystallographical symmetry, and there is a torsional rotation about the C1–C1′ biphenyl link of 27° while one half of the molecule is also internally twisted by 26° [10]. In the other four pigments, which have crystallographically-imposed C_i symmetry, the plane of the terminal (anilide) benzene ring is twisted out of the plane of the biphenyl ring (C1–C6), although in the case of Y83 only by 2°.

In comparison with the previously reported disazo pigments, the Y83 molecule contains a more complex substitution pattern in the terminal anilide ring, with *o*-, *m*-, and *p*-substituents. In this series, Y83 provides the reddest shade. In solution in 1,2,4-trichlorobenzene, Y83 gives a λ_{max} value of 438 nm, 7 nm bathochromic of the parent compound Y12. The molar extinction coefficients for Y83 and Y12 are 6.23×10^{-4} and 6.83×10^{-4} l mol^{-1} cm^{-1} respectively. Consistent with this result, PPP-MO calculations, assuming molecular planarity in each case, predict a lower oscillator strength for Y83 (1.87) compared with Y12 (2.47)

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 (Y83)	Yellow 83	OCH_3	Cl	OCH_3	Cl
1h	Orange 16	H	H	H	OCH_3

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

	x/a	y/b	z/c	U_{eq}/U_{iso}
CL1	1.8886 (8)	0.16026(16)	0.49630(19)	0.0593(22)
CL2	0.3018(8)	0.39003(16)	0.22224(19)	0.0613(20)
O1	1.1489(19)	0.0892(4)	0.1003(5)	0.063(6)
O2	1.3463(17)	0.1843(4)	0.3192(4)	0.051(5)
O3	0.6817(19)	0.2001(4)	0.0853(5)	0.056(6)
O4	0.7346(21)	0.3599(5)	0.3452(5)	0.071(7)
N1	1.7308(22)	0.1027(5)	0.3360(6)	0.042(6)
N2	1.6358(21)	0.0806(4)	0.2656(5)	0.043(6)
N3	1.0574(20)	0.1788(5)	0.2029(5)	0.046(6)
C1	2.3819(23)	0.0159(5)	0.4749(6)	0.034 (3)
C2	2.2569(25)	0.0670(5)	0.5038(7)	0.042 (3)
C3	2.0415(24)	0.0947(5)	0.4568(6)	0.042(3)
C4	1.9484(24)	0.0740(5)	0.3805(6)	0.039(3)
C5	2.0820(27)	0.0228(6)	0.3516(7)	0.046(3)
C6	2.2879(25)	−0.0055(5)	0.3979(6)	0.042(3)
C7	1.4257(24)	0.1051(5)	0.2225(7)	0.041(3)
C8	1.3525(29)	0.0743(7)	0.1449(7)	0.052(3)
C9	1.5268(46)	0.0250(10)	0.1200(11)	0.067(13)
C10	1.2736(26)	0.1594(6)	0.2535(7)	0.048(3)
C11	0.8801(25)	0.2301(6)	0.2126(7)	0.049(3)
C12	0.6849(26)	0.2407(6)	0.1484(7)	0.050(3)
C13	0.5080(31)	0.2892(7)	0.1525(8)	0.052(4)
C14	0.5298(25)	0.3276(5)	0.2193(7)	0.049(3)
C15	0.7220(28)	0.3190(6)	0.2836(7)	0.055(3)
C16	0.9041(27)	0.2691(6)	0.2792(8)	0.052(4)
C17	0.4723(32)	0.2056(8)	0.0208(9)	0.062(10)
C18	0.9526(41)	0.3580(11)	0.4056(11)	0.080(13)
H1	1.669(18)	0.133(4)	0.356(5)	0.00(3)
H2	2.360(24)	0.091(5)	0.558(6)	0.08(4)
H3	1.007(22)	0.153(5)	0.155(5)	0.04(3)
H5	2.005(24)	0.010(5)	0.297(6)	0.07(4)
H6	2.409(22)	−0.037(5)	0.370(5)	0.06(3)
H13	0.381(31)	0.293(6)	0.123(8)	0.10(5)
H16	1.020(27)	0.264(5)	0.322(6)	0.08(4)
H91	1.514(34)	−0.015(7)	0.151(8)	0.10(6)
H92	1.441(24)	0.006(5)	0.080(6)	0.04(4)
H93	1.721(29)	0.025(7)	0.137(8)	0.08(5)
H171	0.454(26)	0.252(5)	−0.003(6)	0.06(4)
H172	0.264(32)	0.208(6)	0.040(7)	0.09(5)
H173	0.532(25)	0.168(5)	−0.007(6)	0.06(4)
H181	1.027(40)	0.396(9)	0.378(11)	0.15(9)
H182	0.925(46)	0.307(10)	0.431(12)	0.21(11)
H183	0.963(32)	0.394(7)	0.434(8)	0.09(6)

[5]. In the solid state, however, Y12 provides significantly lower colour strength than the other pigments, including Y83. This can be explained by the significant deviation from planarity of Y12 molecules in its crystal structure, in comparison with Y83 which is essentially planar. PPP-MO calculations modified to take account of bond

Table 3
Selected intramolecular distances (Å) (e.s.d.s in parentheses)

Bond	Distance
C1–C1′	1.521(23)
C3–CL1	1.744(11)
C14–CL2	1.741(13)
C4–N1	1.383(16)
N1–H1	0.79(8)
N1–N2	1.307(13)
N2–C7	1.309(15)
C7–C8	1.464(16)
C8–O1	1.233(16)
C8–C9	1.454(26)
C7–C10	1.502(17)
C10–O2	1.237(14)
C10–N3	1.358(16)
C12–O3	1.358(14)
O3–C17	1.421(18)
C15–O4	1.338(15)
O4–C18	1.401(22)
N3–H3	0.98(9)
N3–C11	1.418(16)
H1...O2	1.99(9)
H3...O1	1.82(10)
H1...CL1	2.55(8)
H3...O3	2.13(12)

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

Angle	Y83
C1′–C1–C2	120.4(10)
C1–C1–C6	121.7(10)
C4–N1–H1	116(6)
C4–N1–N2	120.9(10)
H1–N1–N2	123(6)
N1–N2–C7	122.8(10)
N2–C7–C8	114.7(10)
C7–C8–O1	121.8(12)
C7–C8–C9	118.7(13)
O1–C8–C9	119.5(12)
N2–C7–C10	121.0(10)
C7–C10–O2	121.7(11)
O2–C10–N3	124.1(11)
C7–C10–N3	114.3(10)
C10–N3–H3	117(6)
C10–N3–C11	128.3(10)
H3–N3–C11	114(6)
C12–O3–C17	118.8(11)
C15–O4–C18	119.9(13)

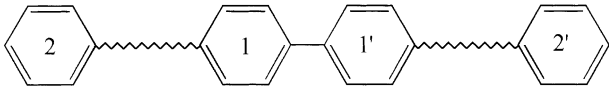

Fig. 2.

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

Angle	
C3–C4–N1–N2	−176.3(11)
N1–N2–C7–C10	−2.4(17)
C7–C10–N3–C11	−177.1(11)
C4–N1–N2–C7	177.9(11)
N2–C7–C10–N3	−178.7(11)
C10–N3–C11–C12	176.5(12)

Table 6
Angles between planes in the crystal structures of Diarylide yellow pigments

Pigment	Angle between planes (°)		
	1 and 2	1 and 1′	1′ and 2′
Y12	2.01	26.71	25.84
Y13	9.03	0	9.03
Y14	7.45	0	7.45
Y63	6.60	0	6.60
Y83	2.62	0	2.62

rotation, have been used to predict that rotation about the biphenyl link in Y12 is likely to cause a hypsochromic shift and a reduction in intensity of the visible absorption band [5].

Y83 provides superior technical performance compared with the other disazo pigments, especially in terms of lightfastness and solvent resistance. It is generally observed that electron releasing substituents in the arylide ring provide improved lightfastness in azoacetoacetanilide pigments. In this respect, Y83 contains two methoxy groups in each ring. The role of the *p*-chloro group, which is electron-withdrawing by virtue of its inductive effect may be associated with determining the colour of the pigment. For example, we have demonstrated previously that electron-withdrawing *p*-substituents can lead to enhanced colour strength in azoacetoacetanilide pigments [11]. Molecules of Y83 show the same type of *intra*molecular hydrogen bonding (O2...H1 is 1.99 Å and O1...H3 is 1.82 Å) as is observed for Y12, Y13, Y14 and Y63. The rather long CL1...H distance (2.55 Å) and the narrow C–CL...H angle (68°) suggests that *intra*molecular hydrogen bonding with chlorine is not significant. Y83 contains an *o*-methoxy group in the anilide ring. From a previously-reported crystal structure determination of C.I. Pigment Yellow 74, an important monoazoacetoacetanilide pigment containing an *o*-methoxy group in the anilide ring, in which hydrogen atoms were not located, intramolecular hydrogen bonding between the methoxy oxygen atom and the amide hydrogen was proposed [12]. The O3...H3 distance in Y83 is 2.13 Å. In our opinion, this distance, taking into account the geometry around O3, is better interpreted as an electrostatic interaction. Nevertheless, the interaction may be a factor in constraining this part of the molecule to a nearly planar conformation. There is evidence in this series of pigments that deviation from molecular planarity causes a weakening of the O1...H3 hydrogen bonding, and we have previously suggested this as a probable factor in explaining the inferior lightfastness of Y12 [7]. The observations that, in this series of pigments, Y83 is the most lightfast, its molecules are the most coplanar within the crystal structure, and atoms O1...H2 have the strongest hydrogen bonding (shortest separation), reinforce this suggestion. However, since hydrogen atoms are not well located by X-ray diffraction, this deduction should be regarded as indicative rather than conclusive.

In the crystal structure of Y83, as with the other Diarylide yellows, there is no *inter*molecular hydrogen bonding. The molecular packing found in Y83 crystals is of a different type to that observed in the other pigments of the series. All of those pigment crystals exhibit an arrangement of interleaved molecules with anti-parallel alignment as illustrated in Fig. 3. There are inversion centres between molecules which are at about one quarter

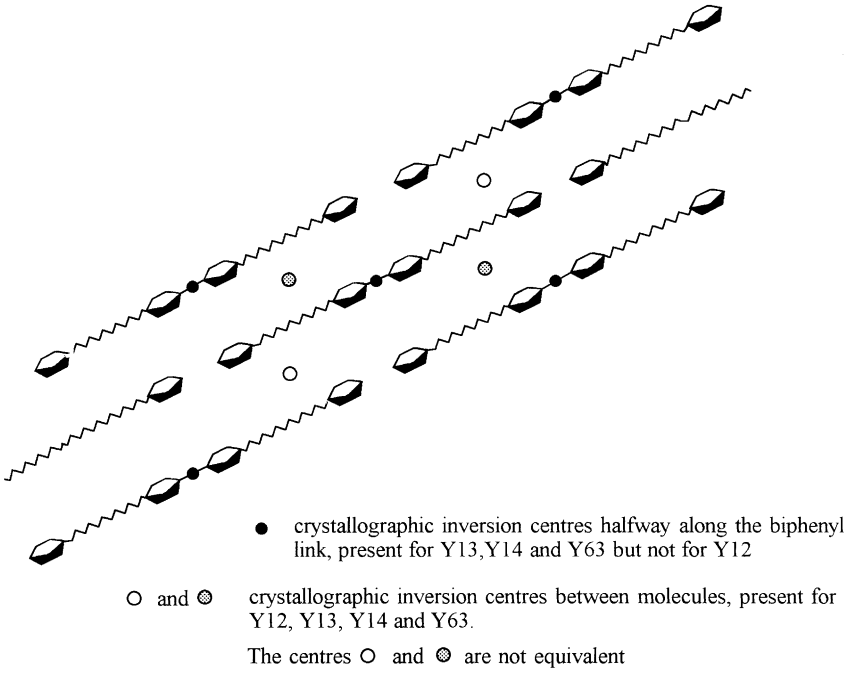

Fig. 3. Interleaved anti-parallel packing of molecules of the type observed in Y12, Y13, Y14 and Y63.

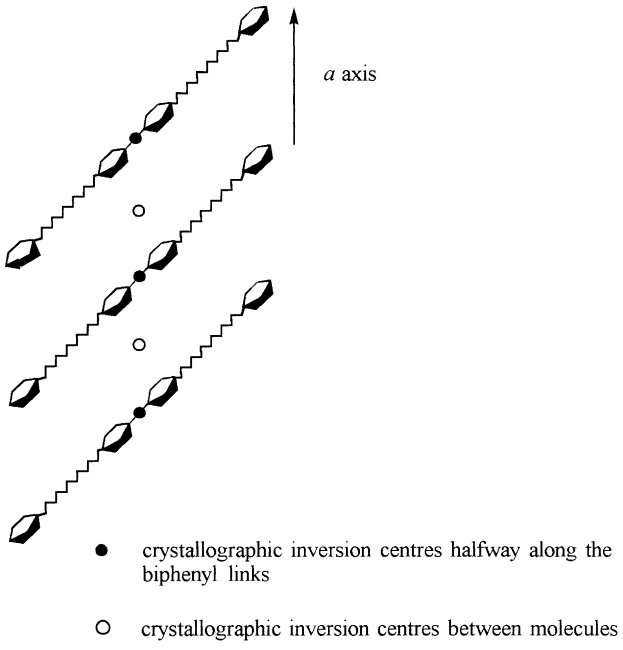

Fig. 4. Inclined stack of Y83 molecules.

and three-quarters of the way along the length of a molecule. The result is that each half of each molecule is anti-parallel to the half molecules immediately above and below, and each molecule in each stack is interleaved between molecules in the adjacent stacks. Y83, however, adopts a simple inclined stacking arrangement as illustrated in Fig. 4. In this case, the above and below relationship between molecules involves a simple unit translation along the short *a* axis. There are crystallographic inversion centres between molecules, but only one inversion centre between each pair of molecules and these inversion centres are close to the centre of the molecule. Their symmetry operation, together with the C_i molecular symmetry, is to reproduce the unit translation along the *a* axis as shown in Fig. 4. The distance between adjacent molecules in the inclined stacks in Y83 is 3.47 Å, as measured by the perpendicular distance between the plane of the ring (C1–C1′) in one molecule and the equivalent plane in a molecule above or below. This gives an angle of 47.2° for the inclination of molecules in the stack with respect to the *a* axis. There are two molecules in the unit cell of Y83 and these are in separate, but symmetry equivalent, stacks of molecules. For Y12, Y13, Y14 and Y63, we measured the distances between molecules in terms of the perpendicular distance between the plane defined by N1, N3 and C8 in one half of one molecule and the corresponding planes in the half-molecules immediately above and below [7]. These distances varied from 3.23 to 3.51 Å, and we tentatively suggested a qualitative correlation between the distances, as a measure of the efficiency of face to face packing, and solvent resistance. In Y83, this distance is 3.21 Å. This might be regarded as consistent with the observation that Y83 exhibits enhanced solvent resistance compared with the other pigments. However, it is acknowledged that the distance is not directly comparable with the others because in Y83 the molecules are translationally related and displaced, while in the other pigments the molecules are inversion related and anti-parallel.

The ability of certain Diarylide yellow pigments to form solid solutions is of technological importance. This is commonly achieved industrially by co-synthesis using mixed azo coupling procedures and may be used to produce pigments with improved colouristic and dispersion properties [13]. C.I. Pigment Yellows 114, 126, 127, 174 and 188 are examples of commercial products of this type, the last of these being a solid solution of Y12 and Y13. It has previously been reported that Y12, Y13, Y14 and Y63 form solid solutions with one another over a wide range of concentrations of the individual components, and the synergistic effects of the solid solutions have been investigated by comparing with physical mixtures of the individual components [13]. On the basis of our single crystal investigations, this is as expected in the case of Y13, Y14 and Y63 since these pigments have essentially identical triclinic crystal structures with interleaved molecular stacking [7]. In contrast, Y12 crystals are monoclinic and the molecules are much more twisted, but they pack together in essentially the same arrangement as for Y13, Y14 and Y63. Assuming that the energy associated with molecular untwisting of Y12 is low, and quantum mechanical calculations have suggested that the energy of the biphenyl molecule is relatively insensitive to rotation about the formal single bond between the rings through a wide range of torsion angle [14], the similarity of the packing provides a simple explanation for the readiness of Y12 to form solid solutions with the other pigments. We have re-investigated this solid solution formation using pigment mixtures prepared both by a mixed coupling process and by co-recrystallisation from 1,2,4-trichlorobenzene. We recorded and analysed the X-ray diffraction profiles for a large number of samples over a wide range of composition and our results confirmed the previous findings [13]. In addition, we have investigated and found no evidence for solid solution formation between Y83 and any of these four pigments. The X-ray powder diffraction patterns of samples, prepared in either way over a range of compositions, invariably showed peaks due to separate species, similar to those of physical mixtures. The structure determination of Y83 has established that the molecular packing is of a very different type, resulting in significant differences in intermolecular interactions, compared with the other pigments, and this provides an explanation for its inability to form solid solutions.

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