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The crystal structure of CI Pigment Yellow 97, a superior performance Hansa yellow pigment

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Abstract

CI Pigment Yellow 97 is one of the most important industrial Hansa yellow monoazo pigments because of its superior technical performance in application. Crystals of this pigment are triclinic. The molecule adopts the ketohydrazone form in its crystal structure and there is strong intramolecular hydrogen bonding. The molecule deviates significantly from planarity. The phenyl ring of the phenylsulfonamide group is positioned like an open lid, making an angle of 52.21(11)° with the arylhydrazone ring. There is also a degree of intermolecular hydrogen bonding between sulfonamide groups in adjacent molecules. The relationship between features seen in the crystal structure and the technical performance of this pigment are discussed, particularly with regard to the role of the phenylsulfonamide group.

Keywords: X-ray crystallography; CI Pigment Yellow 97; Monoazoacetoacetanilide; Hansa Yellow; Ketohydrazone; Arylsulfonamide

1. Introduction

The range of industrial yellow organic pigments is dominated by the azoacetoacetanilides, of both monoazo and disazo types [1–4]. Compounds (**1a**)–(**1k**) represent the most important commercial examples in a long established range of monoazo yellow pigments traditionally known as Hansa Yellows (Table 1). The pigments are synthesised by azo coupling of diazotised aniline derivatives with acetoacetanilide coupling components. These products, in general, are characterised by bright yellow colours of moderate intensity, and good lightfastness but rather poor resistance towards organic solvents. Most of the products tend therefore to be used in applications such as water-based decorative paints where this deficiency is not critical.

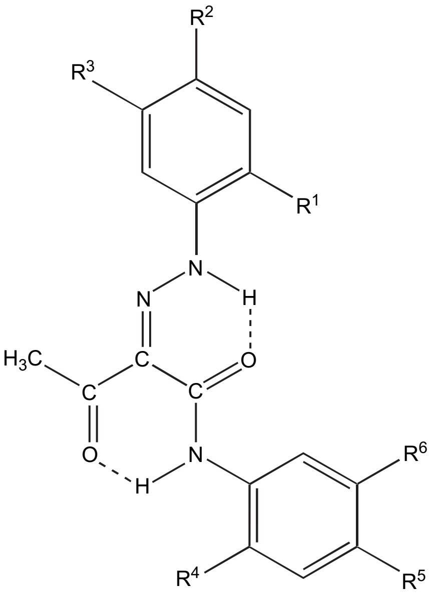

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Table 1
Substituent pattern in monoazoacetoacetanilide pigments

Compound	CI Pigment Yellow	R^1	R^2	R^3	R^4	R^5	R^6
1a (Y1)	1	NO_2	CH_3	H	H	H	H
1b (Y3)	3	NO_2	Cl	H	Cl	H	H
1c (Y6)	6	NO_2	Cl	H	H	H	H
1d (Y65)	65	NO_2	OCH_3	H	OCH_3	H	H
1e	73	NO_2	Cl	H	OCH_3	H	H
1f (Y74)	74	OCH_3	NO_2	H	OCH_3	H	H
1g	75	NO_2	Cl	H	H	OC_2H_5	H
1h (Y97)	97	OCH_3	SO_2NHPh	OCH_3	OCH_3	Cl	OCH_3
1i (Y98)	98	NO_2	Cl	H	CH_3	Cl	H
1j	111	OCH_3	NO_2	H	OCH_3	H	Cl
1k	116	Cl	$CONH_2$	H	H	$NHCOCH_3$	H
1l	–	OCH_3	SO_2NEt_2	H	H	H	H

The X-ray single crystal structures of Y1 (**1a**) [5,6], Y3 (**1b**) [7], Y6 (**1c**) [8,9], Y65 (**1d**) [10], Y74 (**1f**) [11] and Y98 (**1i**) [12] have been reported and the results of the earlier crystallographic studies reviewed [13]. The molecules in all cases exist in the ketohydrazone tautomeric form and most adopt an essentially planar configuration, with the exception of a twisting of up to 20° of the amide phenyl ring in some cases. The good lightfastness which is a characteristic feature of these products has been attributed to the intramolecular hydrogen bonding, which provides electronic and steric protection of the chromophore towards photochemical degradation. The electronic protection results from a reduction in electron density at the hydrazone chromophore, thus reducing susceptibility towards photo-oxidation. The relatively poor resistance to organic solvents in this series of pigments may be explained by the observation that the intermolecular interactions in the crystal structures are weak, in that they involve principally only van der Waals' forces, except that, in the case of Y3 (**1b**), Y65 (**1d**) and Y74 (**1f**), very weak ($C-H\cdots O$) intermolecular H-bonding has been suggested [13]. CI Pigment Yellow 97 (**1h**) is a product of some industrial importance, since it offers superior properties, including excellent colour strength and lightfastness and significantly improved solvent resistance compared with the rest of the Hansa Yellow series, so that it is suitable for a wider range of applications, especially in coatings. The molecule has a complex substituent pattern, containing a phenylsulfonamide group, four methoxy groups and a chloro group. The enhanced properties of this monoazo pigment have been attributed, in general terms, to its larger molecular size and the presence of the phenylsulfonamide group [3,4]. We report in this paper a single crystal X-ray structure determination for this pigment and a discussion of the influence of features of the molecular and crystal structure on its technical performance. In particular, the investigation provides an enhanced understanding of the role of the phenylsulfonamide group in determining the performance of this pigment.

2. Experimental

2.1. Crystallisation

CI Pigment Yellow 97, 2-[(2,5-dimethoxy-4-phenylsulfonamidophenylazo[*N*-(4-chloro-2,5-dimethoxyphenyl)]-3-oxobutanamide)] (**1h**), was supplied by Dominion Colour Corporation, 199 New Toronto St., Toronto, Ontario, Canada as a yellow powder. Crystals suitable for X-ray analysis were obtained by slow cooling from 120 °C of solutions in chlorobenzene.

2.2. Crystal data

The single crystal was covered in nujol and mounted with vacuum grease on a glass fibre on a Bruker AXS P4 diffractometer. Data were collected with Mo K_α radiation (0.7107 Å) at 160 K, cooled by an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were collected for absorption by psi scans. The structure was solved by direct and difference Fourier methods and refined by full-matrix least-square on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic computing was performed with SHELXTL programs. The hydrogen atoms H2N and H4N were located in the difference Fourier map and freely refined.

Crystal data have been deposited as a Crystallographic Information File (CIF) with the Cambridge Crystallographic Data Centre and assigned the deposition number CCDC 276441.

CI Pigment Yellow 97: $C_{26}H_{27}ClN_4O_8S$, $M_r = 591.03$; intense orange crystals $0.72 \times 0.50 \times 0.18$ mm^3; triclinic, $a = 8.5781(8)$, $b = 12.9522(13)$, $c = 13.2828(12)$ Å; $\alpha = 79.451(7)°$, $\beta = 73.815(7)°$, $\gamma = 87.100(8)°$; $V = 1393.3(2)$ Å^3; space group $P\bar{1}$; $Z = 2$, $D_c = 1.409$ Mg m^{-3}, $T = 160(2)$ K; $\lambda = 0.71073$ Å (Mo K_α radiation); $\mu = 0.268$ mm^{-1}. $R1 = 0.0791$, $wR2 = 0.1921$ for $I > 2\sigma(I)$, goodness-of-fit on $F^2 = 1.088$.

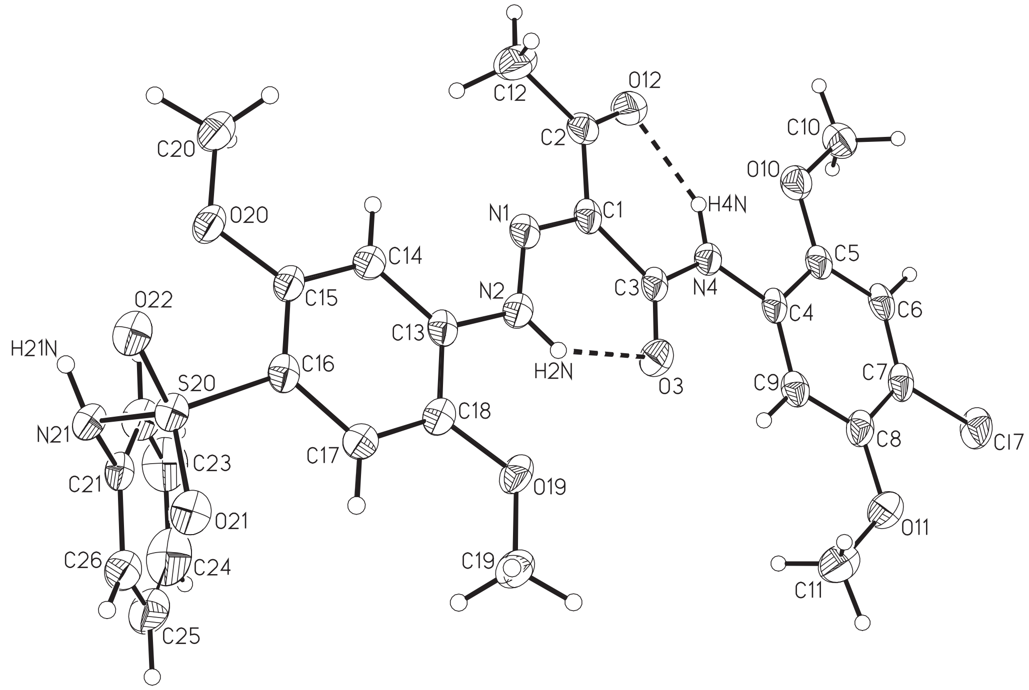

Fig. 1. Molecular structure and atomic labelling scheme for Y97.

3. Results and discussion

Fig. 1 shows the molecular structure and atomic labelling scheme for Y97. Further crystal structure data are given in Tables 2–4. The molecule adopts the ketohydrazone tautomeric form, similar to that of the monoazoacetoacetanilides previously investigated, and shows intramolecular hydrogen bonding typical of these systems. In Y97, the relevant distances (Table 2) are N1–N2, 1.309(3); C1–N1, 1.315(3) Å which fall within the range of distances (1.309–1.335 and 1.298–1.316 Å, respectively) reported for the compounds reviewed by Whitaker [13]. Fawcett et al. have reported the crystal structure of a closely related compound (**1l**) which has no commercial significance to our knowledge [14]. The corresponding bond lengths for **1l** are reported as longer: N–N, 1.341(4); N–C, 1.330(4) Å. The strongest (shortest) hydrogen bonds in Y97 are NH···O intramolecular interactions involving hydrazone N2 and amide O3, amide N4 and ketone O12. The former has the shortest N···O distance [2.568(3) Å] and the angle N2–H2N···O3 is 130(3)°. The hydrogen bond involving N4 is less bent [146(3)°] yet the N···O distance is longer [2.667(3) Å]. This intramolecular hydrogen bonding is typical of that shown by the previously reported Hansa yellow structures [13,14]. The hydrazone N2–H2N

Table 2
Bond lengths [Å] and angles [°] for Y97

C(1)–N(1)	1.315(3)	C(1)–C(2)	1.469(4)	C(1)–C(3)	1.509(4)
N(1)–N(2)	1.309(3)	C(2)–O(12)	1.224(3)	C(2)–C(12)	1.515(4)
N(2)–C(13)	1.395(3)	N(2)–H(2N)	0.83(4)	C(3)–O(3)	1.230(3)
C(3)–N(4)	1.348(3)	N(4)–H(4N)	0.91(3)	S(20)–O(21)	1.428(2)
S(20)–O(22)	1.438(2)	S(20)–N(21)	1.631(2)	C(21)–N(21)	1.435(3)
N(21)–H(21N)	0.86(3)				
N(1)–C(1)–C(2)	113.3(2)	N(1)–C(1)–C(3)	122.6(2)	C(2)–C(1)–C(3)	124.1(2)
N(2)–N(1)–C(1)	121.4(2)	O(12)–C(2)–C(1)	122.3(2)	O(12)–C(2)–C(12)	119.1(3)
C(1)–C(2)–C(12)	118.6(2)	N(1)–N(2)–C(13)	119.4(2)	N(1)–N(2)–H(2N)	122(3)
C(13)–N(2)–H(2N)	118(3)	O(3)–C(3)–N(4)	124.7(2)	O(3)–C(3)–C(1)	120.0(2)
N(4)–C(3)–C(1)	115.2(2)	C(3)–N(4)–H(4N)	112.1(19)	C(4)–N(4)–H(4N)	120.2(19)
O(21)–S(20)–O(22)	117.86(11)	O(21)–S(20)–N(21)	108.75(11)	O(22)–S(20)–N(21)	105.72(11)
O(21)–S(20)–C(16)	106.82(12)	O(22)–S(20)–C(16)	110.92(12)	N(21)–S(20)–C(16)	106.19(11)
S(20)–N(21)–H(21N)	107(2)				

Table 3
Torsion angles [°] for Y97

C(2)−C(1)−N(1)−N(2)	179.4(2)	C(3)−C(1)−N(1)−N(2)	0.4(4)
N(1)−C(1)−C(2)−O(12)	−174.6(3)	C(3)−C(1)−C(2)−O(12)	4.3(4)
N(1)−C(1)−C(2)−C(12)	5.2(4)	C(3)−C(1)−C(2)−C(12)	−175.9(3)
C(1)−N(1)−N(2)−C(13)	−176.7(2)	N(1)−C(1)−C(3)−O(3)	−2.6(4)
C(2)−C(1)−C(3)−O(3)	178.6(2)	N(1)−C(1)−C(3)−N(4)	177.8(2)
C(2)−C(1)−C(3)−N(4)	−1.0(4)	O(3)−C(3)−N(4)−C(4)	−1.9(4)
C(1)−C(3)−N(4)−C(4)	177.6(2)	C(9)−C(4)−N(4)−C(3)	3.6(4)
C(5)−C(4)−N(4)−C(3)	−176.1(2)	C(15)−C(16)−S(20)−N(21)	64.9(2)
C(17)−C(16)−S(20)−N(21)	−109.2(2)	O(22)−S(20)−N(21)−C(21)	165.37(18)
C(16)−S(20)−N(21)−C(21)	47.5(2)	C(26)−C(21)−C(22)−C(23)	0.3(4)

makes another much longer NH···O contact involving the methoxy O19 which is very bent [107(3)°] at H2N and the N···O distance is 2.632(3) Å.

It is of interest that, in contrast to the traditional Hansa Yellows, the molecules of Y97 deviate significantly from planarity. This pigment is unique in the range of industrial azo pigments in that it contains an arylsulfonamide group. The phenyl ring of the sulfonamide group is positioned like an open lid over the central dimethoxy aromatic ring such that the angle between planes C13−C18 and C21−C26 is 52.21(11)°. It is conceivable that this feature contributes towards the good lightfastness of this pigment. It has been suggested, in the case of some textile reactive dyes, that the arylsulfonamide ring is capable of acting as an UV filter which leads to improved lightfastness properties [15]. It is significant that the group is not in the same plane as, and hence not conjugated with, the chromophore, so that energy transfer from the UV filter to the chromophore is minimised. Incorporation of arylsulfonamide groups into acid dyes has also been reported to lead in some cases to improved dyeing properties, including lightfastness, on polyamide and wool [16]. In the other section of the Y97 molecule there is a slight bend between the central dimethoxy-substituted aromatic ring (C13−C18) and the plane determined by the hydrazonoarylamide sytem (N1, N2, C1, C3, N4, C4−C9) where the angle between the planes is 7.42 (11)°. The central region of the molecule, containing the intramolecular hydrogen bonding network is itself planar. None of the non-hydrogen atoms deviate very significantly from the plane (N1, N2, C1, C2, O12, C3, O3, N4) where the rms deviation of the fitted atoms is 0.0247 Å and C2 has the largest deviation at −0.0393(21) Å., closely followed by O12 at 0.0367(17) Å.

Table 4
Hydrogen bonds for Y97 [Å and °]

D−H···A	*d*(D−H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(2)−H(2N)···O(3)	0.83(4)	1.95(4)	2.568(3)	130(3)
N(2)−H(2N)···O(19)	0.83(4)	2.27(4)	2.632(3)	107(3)
N(4)−H(4N)···O(12)	0.91(3)	1.86(3)	2.667(3)	146(3)
N(21)−H(21N)···O(22A)	0.86(3)	2.10(4)	2.931(3)	163(3)
N(21)−H(21N)···O(20)	0.86(3)	2.72(3)	3.152(3)	112(2)
C(19)−H(19)···O(21B)	0.98	2.58	2.995(3)	105.8

Symmetry transformations used to generate equivalent atoms. A: $-x-1, -y, -z+1$ for O21B, B: $-x-1, -y+1, -z+1$.

It has been established, for a wide range of chemical types of pigment, that intermolecular hydrogen bonding is an important feature in providing enhanced technical performance [17,18]. A notable feature of the crystal structure of Y97 is that there is significant intermolecular H-bonding between two sulfonamide group of the form N21−H21N···O22A, as illustrated in Fig. 2, where the N···O distance is 2.931(3) Å and the angle at H21N is 163(3)°. This gives a dimeric motif resulting in the formation of an eight membered ring, similar to that commonly seen in carboxylic acids. The sulfonamide groups are thereby held in a head-to-head arrangement. It is likely that this intermolecular interaction contributes significantly to the enhanced solvent resistance of this pigment, and conceivably also to the lightfastness properties. There is a weaker CH···O hydrogen bonding involving C19 and O21B, the other sulfonamide O atom, where the C···O distance is 2.995(3) Å and the angle at H19B is 105°. The CH···O and NH···O interactions combined, propagate a chain roughly parallel to the *b* axis. As for $\pi-\pi$ interactions, these are less apparent as the closest intermolecular centroid−centroid distance is 3.6850(16) Å between the two dimethoxy-substituted rings (C4−C9 and C13−C18) in different molecules.

4. Conclusions

The X-ray single crystal structure of CI Pigment Yellow 97 illustrates that it exists as a ketohydrazone with strong intramolecular hydrogen bonding typical of this class of monoazo pigment. The presence of the phenylsulfonamide group, which is unusual in the range of commercial organic pigments, appears to play a vital role in determining the superior technical performance of this pigment by participating in intermolecular hydrogen bonding and, conceivably, by providing UV protection by its orientation with respect to the chromophore. The data obtained from this study and the concepts developed, as well as providing enhanced understanding of the performance of this pigment, offer

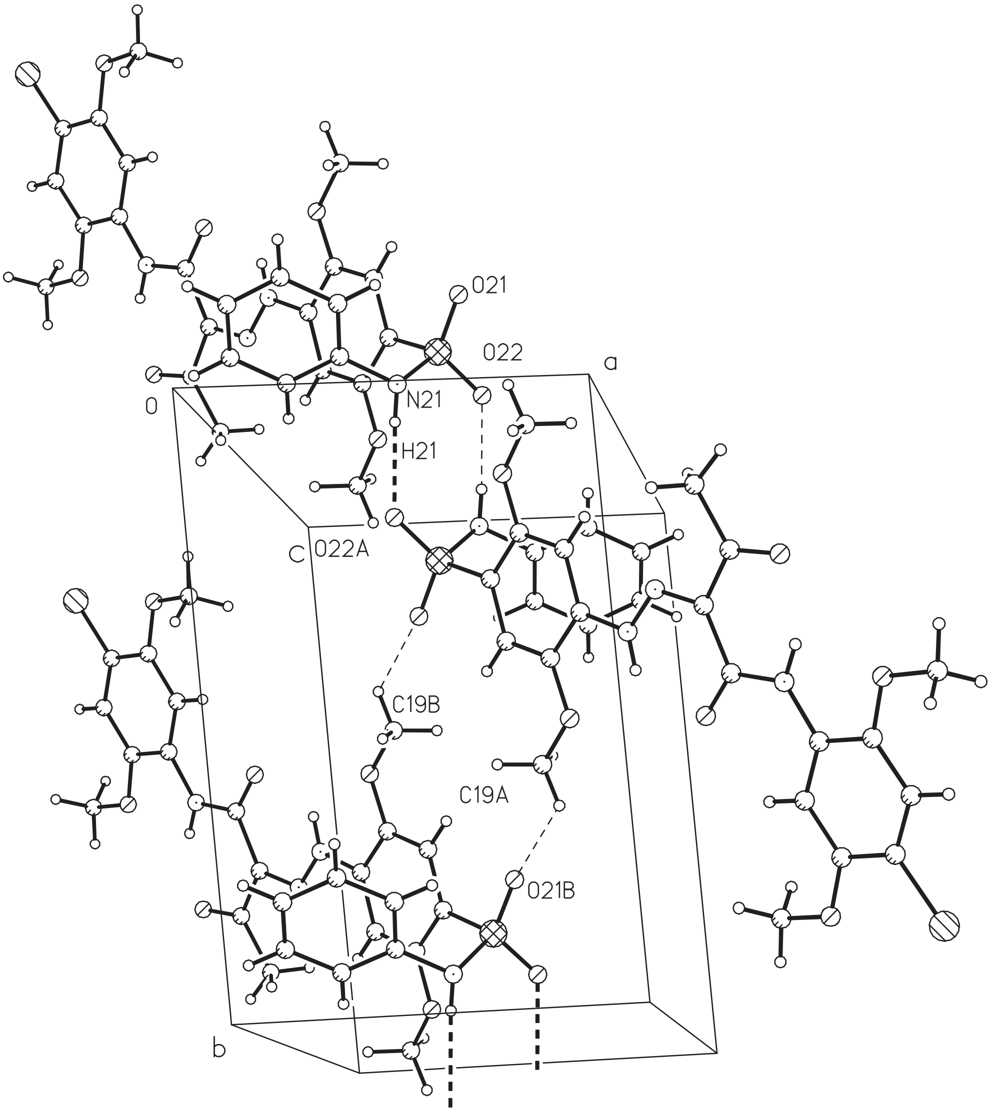

Fig. 2. NH···O and CH···O intermolecular hydrogen bonding in Y97.

considerable potential for the design by crystal engineering of new organic pigments with improved performance.

Acknowledgements

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