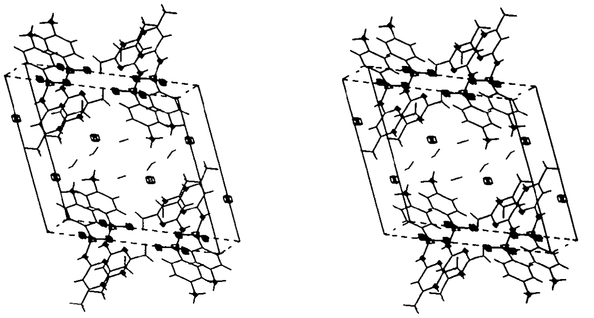

Fig. 2. Stereoview of the packing in the unit cell, viewed approximately along **c**. Unit-cell edges are indicated by a solid line for **a**, and dashed lines for **b**. N atoms are designated by tetrahedral symbols, O atoms by octahedra and Cl atoms by cubes. Drawing made by program *PACK* (Swanson, Rosenfield & Meyer, 1982).

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583 Pigment Yellow GG, A Mixed Crystal of α-(4-Chloro-2-nitrophenylhydrazono)-acetoacetanilide (CI Pigment Yellow 6) and α-(2-Nitrophenylhydrazono)acetoacetanilide (α-CI Pigment Yellow 5)

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Abstract. Monoclinic, $P2_1/n$, $a = 7{\cdot}572\,(4)$, $b = 20{\cdot}366\,(4)$, $c = 10{\cdot}413\,(3)$ Å, $\beta = 98{\cdot}89\,(3)°$, $V = 1586{\cdot}5\,(0{\cdot}9)$ Å^3, $Z = 4$, $D_m = 1{\cdot}447\,(5)$ Mg m^{-3}. Assuming $C_{16}H_{13}ClN_4O_4$ ($M_r = 360{\cdot}76$), $D_x = 1{\cdot}510\,(1)$ Mg m^{-3}, $F(000) = 744$, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}22$ mm^{-1}. $R = 6{\cdot}5\%$ for 3123 non-zero intensities (room temperature). The structure was found to be a mixture of CI Pigment Yellow 6 ($C_{16}H_{13}ClN_4O_4$) ($0{\cdot}605 \pm 0{\cdot}003$) and α-CI Pigment Yellow 5 ($C_{16}H_{14}N_4O_4$). The molecule exists as the hydrazone tautomer and three intramolecular hydrogen bonds keep it approximately planar. The molecules are linked by van der Waals forces. The present structure is compared with four other pigment structures and it is concluded that it is a mixed crystal of CI Pigment Yellow 6 in α-CI Pigment Yellow 5 rather than *vice versa*.

Introduction. Pigments colour in the form of discrete crystalline particles. In view of this the colour properties depend not only upon the absorption properties of the molecule but also upon their crystallographic arrangement. This article is one of a group (Whitaker, 1983*a*,*b*, 1984*a*,*b*, 1985*a*,*b*; Whitaker & Walker, 1985) concerned with the structure of acetoacetanilide azo-pigments with the long-term aim of relating colour and crystal structure in pigments.

583 Pigment Yellow GG (commercially manufactured by Horace Cory & Co.) is nominally CI Pigment Yellow 6, $C_{16}H_{13}ClN_4O_4$, (CI 11670); the

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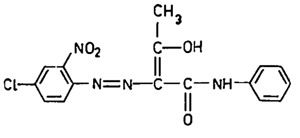
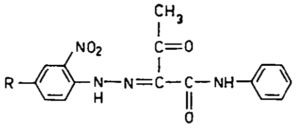
structure of the latter has already been determined (Whitaker, 1983*b*). However, inspection of X-ray powder patterns indicated that the structure of the title pigment was different from that already reported and it was tentatively assumed that the title pigment was a second polymorph. The formula of CI Pigment Yellow 6 is usually given as (I) but previous structure determinations indicated that 'azo-pigment', as applied to this group of pigments, is a misnomer; the azo bond is, in fact, a hydrazone bond (II, $R = \mathrm{Cl}$). This conclusion has been confirmed by other investigators (Paulus, Rieper & Wagner, 1983; Brown & Yadav, 1984; Paulus, 1984). During the course of the structure determination evidence emerged that 583 Pigment Yellow GG was not pure CI Pigment Yellow 6 (II, $R = \mathrm{Cl}$) but a mixed crystal of this and CI Pigment Yellow 5, $C_{16}H_{13}N_4O_4$, (II, $R = \mathrm{H}$) (CI 11660).



(I)



(II)

Experimental. Single crystals were obtained by the slow cooling of a hot saturated toluene solution. Some of the crystals were blades with a monoclinic aspect. The colour, morphological monoclinic angle and extinction directions are different from those reported for CI Pigment Yellow 6 (Whitaker, 1983*c*).

A crystal of size 0·60 × 0·20 × 0·32 mm was used for intensity measurements on an Enraf–Nonius CAD-4 automatic four-circle diffractometer (Mo $K\alpha$ radiation). Least-squares analysis on 25 reflections, with θ range 13·01–14·96°, gave the lattice parameters. Space group $P2_1/n$, with a parallel to the length of the blade and b perpendicular to the blade face. Intensities corrected for absorption (North, Phillips & Mathews, 1968; linear absorption coefficient $0{\cdot}22\ \mathrm{mm}^{-1}$, max., min. transmission factors 0·990, 0·905) and Lorentz–polarization to give 3123 unique reflections of non-zero intensity with $0 \le h \le 9$, $0 \le k \le 24$ and $-12 \le l \le 12$. All were considered observed. Maximum $2\theta = 50{\cdot}0°$. Three standard reflections were used ($\bar{1}66$, $\bar{3}8\bar{4}$, $\bar{4}84$); variations in F (as supplied by the Diffractometer Service) for 41 sets of measurements were respectively 26·69 to 27·74, 39·37 to 40·53 and 30·94 to 33·05. No corrections for secondary extinction.

At a later stage in the investigation the density was measured by flotation: $1{\cdot}447 \pm 0{\cdot}005\ \mathrm{Mg\,m^{-3}}$. On the assumption that this pigment was a 'mixed crystal', the other component would most probably be another related pigment, either CI Pigment Yellow 1 (II, $R = \mathrm{CH_3}$) or CI Pigment Yellow 5 (II, $R = \mathrm{H}$). On this assumption the observed density corresponds to a proportion of 0·74 ± 0·06 of CI Pigment Yellow 1 in CI Pigment Yellow 6 or 0·44 ± 0·03 of CI Pigment Yellow 5 in CI Pigment Yellow 6.

Attempts to solve the structure from that reported for CI Pigment Yellow 6 (Whitaker, 1983*b*) failed. The structure was solved using direct methods.

The refinement of the structure based on F included a weighting function w such that $1/w = (\sigma^2 + gF^2)$; σ was obtained from the diffractometer counting statistics, g was refined as a parameter, final value 0·01294.

Initially the structure was refined assuming the formula of CI Pigment Yellow 6. H atoms found from difference Fourier synthesis confirmed the hydrazone tautomer. These were included with the isotropic temperature factors of the adjacent heavy atom at a distance of 1·05 Å and the refinement completed. It was noticed that the temperature factors for the Cl were higher than expected and an electron density map indicated a very low peak for the Cl.

At this stage the density was measured and found to be significantly low. Consequently the occupancy of the Cl atom was included in the refinement. Further difference Fourier maps indicated the position of the hydrogens and also suggested that the second molecule could not be CI Pigment Yellow 1. In the final refinement the occupancy of Cl was refined and the occupancy of H(3) [II, $R = \mathrm{H(3)}$ for CI Pigment Yellow 5] was included by trial and error until the two occupancies summed to unity (the numbering of the atoms is in Fig. 1). Refinement was carried out until the shifts were less than one-tenth the appropriate standard deviation.

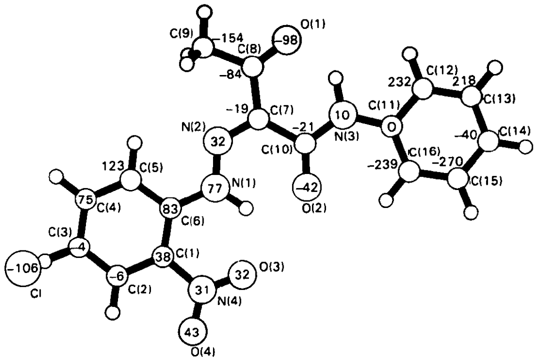


Fig. 1. Structure of the composite molecule projected on to the plane containing C(3), C(4) and C(14). The deviations of the atoms (in 10^{-3} Å) from the weighted least-squares plane of the molecules are also given. The e.s.d.'s of these deviations are 0·001 Å for Cl and a mean of 0·002 Å for the lighter atoms.

No attempt was made to refine the parameters associated with the H atoms except those associated with C(9). Final residual 6·5%, occupancy of Cl 0·605 ± 0·003 compared with 0·56 ± 0·03 from measured density. The final coordinates together with the isotropic temperature factors are given in Table 1.* The maximum values in final difference Fourier synthesis were 0·46 and −0·31 e Å^{-3} respectively. Atomic scattering factors as supplied within program *SHELX*76 (Sheldrick, 1976).

A chlorine analysis was made on the bulk pigment (there being an insufficient number of crystals); this corresponds to 0·42 ± 0·03 of CI Pigment Yellow 6. This confirms a mixed crystal structure but this value is lower than the other two, perhaps owing to the purifying effect of recrystallization.

During computing, programs of the Cambridge Crystallography Package *SHELX*76 (Sheldrick, 1976) were used for data processing, Fourier synthesis, least-squares refinements and the calculation of atomic distances and angles; *PARST* (Nardelli, 1982) was used for the calculation of weighted least-squares planes of the molecule. Figs. 1 and 2 were drawn by *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Tables of bond lengths and angles (Table 2) show, by comparison with accepted bond lengths (*International Tables for X-ray Crystallography*, 1968), that the hydrazone tautomer is the better fit. Fig. 1 gives the proposed structure projected on to the plane containing C(3), C(4) and C(14). The intramolecular distances N(1)–O(2), N(1)–O(3) and N(3)–O(1) suggest intramolecular hydrogen bonds. These have been found in related structures.

The bond length C(3)–Cl is significantly smaller than one would expect from that obtained in other acetoacetanilide pigments (Whitaker, 1983*a*,*b*, 1984*b*). This could be because the position of C(3) (and all atoms except Cl) is a mean from two molecules while the Cl is associated with only one. With this exception there would appear to be no abnormal bond lengths, although a few differ in value by slightly more than 3σ when compared with those from CI Pigment Yellow 6 (Whitaker, 1983*b*).

The molecule is almost planar although all atoms show significant deviation from these planes. Fig. 1 gives the deviations from the weighted least-squares plane through all non-hydrogen atoms. In general these are less than the corresponding deviations in CI Pigment Yellow 6 (Whitaker, 1983*b*) and this is confirmed by a calculation of the root-mean-square

Table 1. *Parameters and standard deviations after anisotropic refinement*

$U_{eq} = \exp[-8\pi^2U(\sin^2\theta)/\lambda^2 \times 10^{-3}]$ (Cruickshank, 1956).

	x	y	z	U_{eq}(Å^2)
C(1)	0·4847 (3)	0·4661 (1)	0·7541 (2)	45 (1)
N(4)	0·5159 (3)	0·5367 (1)	0·7695 (2)	54 (1)
O(3)	0·4458 (3)	0·5738 (1)	0·6857 (2)	72 (1)
O(4)	0·6139 (3)	0·5554 (1)	0·8660 (2)	86 (1)
C(2)	0·5643 (3)	0·4254 (1)	0·8557 (2)	51 (1)
C(3)	0·5408 (3)	0·3590 (1)	0·8480 (2)	53 (1)
Cl*	0·6288 (2)	0·3078 (1)	0·9702 (1)	80 (1)
C(4)	0·4411 (3)	0·3324 (1)	0·7374 (2)	58 (1)
C(5)	0·3628 (3)	0·3719 (1)	0·6371 (2)	52 (1)
C(6)	0·3796 (3)	0·4397 (1)	0·6432 (2)	42 (1)
N(1)	0·2931 (2)	0·4787 (1)	0·5427 (2)	45 (1)
N(2)	0·1880 (2)	0·4483 (1)	0·4471 (2)	43 (1)
C(7)	0·0967 (3)	0·4811 (1)	0·3504 (2)	41 (1)
C(8)	−0·0137 (3)	0·4371 (1)	0·2561 (2)	47 (1)
C(9)	−0·0148 (3)	0·3652 (1)	0·2850 (3)	68 (1)
O(1)	−0·1042 (3)	0·4585 (1)	0·1574 (2)	64 (1)
C(10)	0·1028 (3)	0·5540 (1)	0·3381 (2)	41 (1)
O(2)	0·1900 (2)	0·5874 (1)	0·4245 (1)	52 (1)
N(3)	0·0091 (3)	0·5784 (1)	0·2281 (2)	45 (1)
C(11)	−0·0142 (3)	0·6445 (1)	0·1876 (2)	42 (1)
C(12)	−0·0977 (3)	0·6538 (1)	0·0604 (2)	52 (1)
C(13)	−0·1298 (3)	0·7169 (1)	0·0123 (2)	60 (1)
C(14)	−0·0814 (3)	0·7703 (1)	0·0901 (2)	57 (1)
C(15)	0·0011 (4)	0·7610 (1)	0·2160 (2)	56 (1)
C(16)	0·0370 (3)	0·6983 (1)	0·2654 (2)	51 (1)

* Occupancy factor for Cl = 0·605 ± 0·003.

Table 2. *Bond lengths* (Å) *and angles* (°)

O(3)–N(4)	1·212 (3)	C(8)–C(9)	1·495 (4)
O(4)–N(4)	1·215 (3)	C(7)–C(10)	1·492 (3)
N(4)–C(1)	1·462 (3)	C(10)–O(2)	1·235 (2)
C(1)–C(2)	1·404 (3)	C(10)–N(3)	1·346 (3)
C(2)–C(3)	1·365 (4)	N(3)–C(11)	1·413 (3)
C(3)–Cl	1·700 (3)	C(11)–C(12)	1·390 (3)
C(3)–C(4)	1·386 (4)	C(12)–C(13)	1·386 (4)
C(4)–C(5)	1·378 (3)	C(13)–C(14)	1·372 (4)
C(5)–C(6)	1·387 (3)	C(14)–C(15)	1·375 (3)
C(6)–C(1)	1·404 (3)	C(15)–C(16)	1·387 (3)
C(6)–N(1)	1·394 (3)	C(16)–C(11)	1·382 (3)
N(1)–N(2)	1·328 (2)	N(1)–O(2)	2·593 (3)
N(2)–C(7)	1·313 (3)	N(1)–O(3)	2·601 (3)
C(7)–C(8)	1·487 (3)	N(3)–O(1)	2·654 (3)
C(8)–O(1)	1·225 (3)		
O(4)–N(4)–O(3)	122·9 (0·2)	C(8)–C(7)–C(10)	124·4 (0·2)
O(3)–N(4)–C(1)	119·1 (0·2)	C(10)–C(7)–N(2)	123·6 (0·2)
C(1)–N(4)–O(4)	117·9 (0·2)	C(7)–C(8)–C(9)	118·5 (0·2)
N(4)–C(1)–C(6)	121·9 (0·2)	C(9)–C(8)–O(1)	119·6 (0·2)
C(6)–C(1)–C(2)	121·1 (0·2)	O(1)–C(8)–C(7)	121·6 (0·2)
C(2)–C(1)–N(4)	117·0 (0·2)	C(7)–C(10)–N(3)	114·9 (0·2)
C(1)–C(2)–C(3)	120·2 (0·2)	N(3)–C(10)–O(2)	124·6 (0·2)
C(2)–C(3)–C(4)	119·1 (0·2)	O(2)–C(10)–C(7)	120·4 (0·2)
C(4)–C(3)–Cl	118·8 (0·2)	C(10)–N(3)–C(11)	129·1 (0·2)
Cl–C(3)–C(2)	122·1 (0·2)	N(3)–C(11)–C(16)	124·8 (0·2)
C(3)–C(4)–C(5)	121·1 (0·2)	C(16)–C(11)–C(12)	119·7 (0·2)
C(4)–C(5)–C(6)	121·4 (0·2)	C(12)–C(11)–N(3)	115·6 (0·2)
C(5)–C(6)–C(1)	117·1 (0·2)	C(11)–C(12)–C(13)	120·0 (0·2)
C(1)–C(6)–N(1)	122·7 (0·2)	C(12)–C(13)–C(14)	120·3 (0·2)
N(1)–C(6)–C(5)	120·3 (0·2)	C(13)–C(14)–C(15)	119·7 (0·2)
C(6)–N(1)–N(2)	117·0 (0·2)	C(14)–C(15)–C(16)	120·9 (0·2)
N(1)–N(2)–C(7)	121·4 (0·2)	C(15)–C(16)–C(11)	119·5 (0·2)
N(2)–C(7)–C(8)	112·0 (0·2)		

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and short intermolecular distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43101 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

deviations, 0·189 Å for CI Pigment Yellow 6 and 0·114 Å for the title compound. Alternatively, the distortion may be assessed by comparing the angles between the two benzene groups; these are 18·83 ± 0·07° for CI Pigment Yellow 6 (Whitaker, 1983*b*) and 9·09 ± 0·10° for the title compound. Thus it appears that the mean molecule is less distorted in the present case.

The *a*-axis projection of the structure (Fig. 2) shows that the molecules lie in columns parallel to this axis; adjacent molecules within the columns are antiparallel. The weighted molecular plane is 4·94 ± 0·02° from being parallel to the (101) plane. The molecule is not perpendicular to the column axis, as the normal to the weighted molecular plane is 28·82 ± 0·01° offset with respect to it. All intermolecular distances below 3·50 Å were calculated. The shortest distance, 3·315 ± 0·003 Å, suggests that the intermolecular bonding is due to van der Waals forces.

Comparison with other acetoacetanilide pigments. The crystal structures of several acetoacetanilide pigments are similar as has previously been commented. Mez (1968) and Paulus (1984) stated that CI Pigment Yellow 1 and CI Pigment Yellow 6 were isomorphous, but Whitaker (1984*a*) concluded that the two structures were not, strictly speaking, isomorphous. However, Hansa Yellow 5G (a mixed crystal) is isomorphous with CI Pigment Yellow 1 (Whitaker, 1985*a*) and α-CI Pigment Yellow 5 is also isomorphous with CI Pigment Yellow 1 (Whitaker, 1985*b*). The question is whether the present structure is isomorphous with either α-CI Pigment Yellow 5 or CI Pigment Yellow 6.

Consider the molecular packing within the crystal structure; in all cases the molecules are essentially planar and they are stacked in columns parallel to the *a* axis. The angles between the molecular plane and column axis have been calculated and so have the angles between the molecular plane and the unique (*b*) axis (Table 3). In both cases the angles indicate that the molecules of CI Pigment Yellow 6 are stacked slightly differently from all the others, both within the column of molecules and with respect to the unique axis of the unit cell. Thus the crystal structure indicates that the present structure is isomorphous with α-CI Pigment Yellow 5, as well as Hansa Yellow 5G and CI Pigment Yellow 1, but CI Pigment Yellow 6 is not isomorphous with the others. It follows that, in spite of its composition, 583 Pigment Yellow GG should be thought of as a mixed crystal of CI Pigment Yellow 6 (60%) in α-CI Pigment Yellow 5 (40%) rather than *vice versa*.

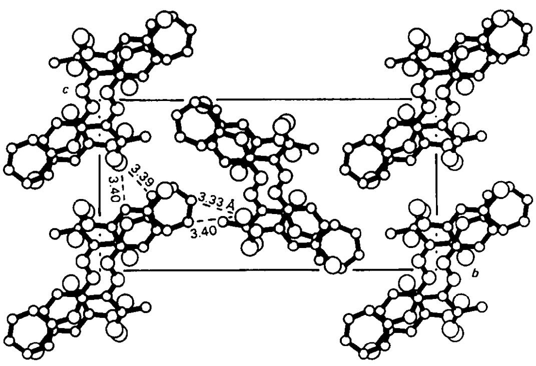

Fig. 2. The packing of 583 Pigment Yellow GG in the unit cell, *a*-axis projection.

Table 3. *Angles* (°) *between the weighted least-squares molecular plane and the column axis of packing* (*a*) *and the unique axis of the crystal* (*b*)

	Column axis of packing	Unique axis of crystal
CI Pigment Yellow 6 (Whitaker, 1983*b*)	27·00 (1)	72·24 (1)
583 Pigment Yellow GG (These results)	28·82 (1)	85·34 (2)
CI Pigment Yellow 5 (Whitaker, 1985*a*)	29·58 (1)	79·59 (2)
Hansa Yellow 5G (Whitaker, 1985*b*)	29·22 (1)	85·35 (2)
CI Pigment Yellow 1 (Whitaker, 1984*a*)	29·50 (7)	86·26 (12)
CI Pigment Yellow 1 (Brown & Yadav, 1984)	29·45 (3)	86·54 (2)
CI Pigment Yellow 1 (Paulus, 1984)	29·41 (1)	86·52 (1)

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