short intramolecular contact (2·50 Å) between C9 and HN10.

The pyramidal character of N10 is rather well marked: it lies 0·19 Å out of the plane defined by C1, C11 and HN10. However, there seems to be a partial conjugation with the central phenyl ring, suggested by the short C1—N10 bond [1·399 (4) Å] and the low value of the torsion angle C2—C1—N10—HN10 : 10(1)°.

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CI Pigment Yellow 60, 4-(2-Chlorophenylhydrazono)-3-methyl-1-phenyl-5-pyrazolone

BY A. WHITAKER

Department of Physics, Brunel University, Uxbridge, Middlesex, England

Abstract. $C_{16}H_{13}ClN_4O$, $M_r = 312 \cdot 76$, triclinic, $P\bar{1}$, $a = 11 \cdot 1256$ (10), $b = 9 \cdot 4507$ (8), $c = 7 \cdot 5798$ (9) Å, $\alpha = 80 \cdot 708$ (9), $\beta = 84 \cdot 382$ (9), $\gamma = 68 \cdot 451$ (7)°, $V = 730 \cdot 9$ (2) Å^3, $Z = 2$, $D_x = 1 \cdot 4211$ (3), $D_m = 1 \cdot 420$ (3) Mg m^{-3}, Cu $K\alpha$, $\lambda = 1 \cdot 54184$ Å, $\mu = 2 \cdot 26$ mm^{-1}, $F(000) = 324$, room temperature, $R = 0 \cdot 082$ for 2773 independent non-zero intensities. The planar molecule exists as the hydrazone tautomer with three intramolecular hydrogen bonds, one very weak. The molecules are linked by van der Waals forces into columns parallel to **b**.

Introduction. Some years ago, with the long-term aim of relating crystal structure and colour, work was published on the structure determination of several azo-pigments involving β-naphthol (Grainger & McConnell, 1969; Kobelt, Paulus & Kunstmann, 1972, 1974; Whitaker, 1977*a,b*, 1978*b*). A review (Whitaker, 1978*a*) of these six crystal structures concluded that for this group of pigments, the azo group was, in reality, a hydrazone group. Further crystal structure determinations (Whitaker, 1980, 1981; Paulus, 1982) on other members of this group of pigments supported this view.

Interest then moved to azo-pigments involving acetoacetanilide and again a series of crystal structures were determined (Whitaker, 1983*a,b*; Paulus, Rieper &

Wagner, 1983; Brown & Yadav, 1984; Whitaker, 1984*a*; Paulus, 1984; Whitaker, 1984*b*, 1985*a*; Whitaker & Walker, 1985; Whitaker, 1985*b*, 1986; Whitaker & Walker, 1987; Whitaker, 1987). The general conclusion from these was that this group of compounds should be classed as hydrazone rather than azo-pigments (Whitaker, 1988).

A third group of 'azo-pigments' are those involving pyrazolone. [General formula (I) according to the *Colour Index* (1971).] The structure of one member of this group, 4-(4-chlorophenylazo)-3-methyl-1-phenyl-5-pyrazolone, has been determined by Golinski, Reck & Kutschabsky (1982) who claimed that the molecule exists in the hydrazone form.

(I)
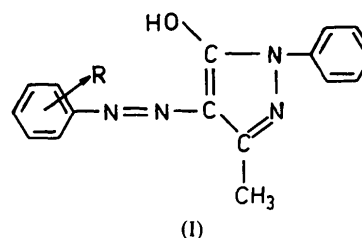
However, the quality of the work was poor, the residual was 13·7%, no direct evidence of the positions

of the hydrogen atoms was obtained and the errors in the bond lengths were generally 0·02–0·03 Å. As further evidence of the quality, one may consider the range of bond lengths in the two phenyl groups; for one this is 1·39 (2) to 1·56 (2) Å and for the other 1·37 (2) Å to 1·51 (2) Å; also, the three aliphatic C–C single bonds are given as 1·46 (2), 1·54 (2) and 1·57 (2) Å. With such errors and such ranges of equivalent bonds it would appear unwise to diagnose azo or hydrazono bonding solely on the basis of this structure determination. Hence, the reason for the present work.

CI Pigment Yellow 60 (CI No. 12705) is a commercially available pigment used in paints, lacquers, printing inks, stains and also for colouring plastics, rubber, paper and floor coverings. It is an 'azo-pigment' with the usual given formula (II) but it is not known whether it is an azo-pigment (II) or (III) [(III) is given by Lewis (1985)] or a hydrazone pigment (IV).

(II)

(III)

(IV)
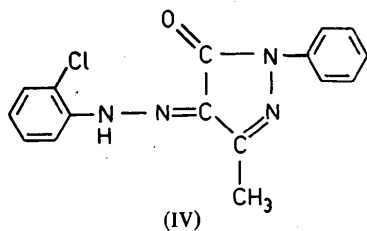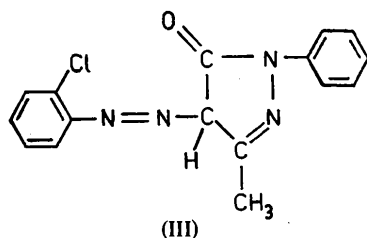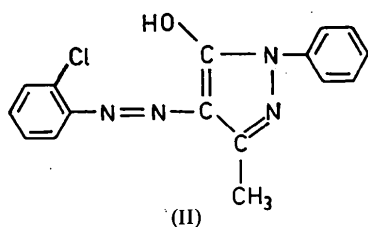
Experimental. The crystals were obtained by the slow cooling of a hot (358 K) saturated toluene solution of the commercial pigment Hansa Yellow 4R. The crystal used for intensity measurements was 0·65 × 0·25 × 0·22 mm. The intensity data were collected using an Enraf–Nonius CAD-4 automatic four-circle diffractometer of the National X-ray Diffractometer Service, nickel-filtered copper radiation and $\omega/2\theta$ scans. Least-squares analysis of 25 reflections, with θ range 20·78 to 39·53°, gave the lattice parameters. Intensities corrected for absorption (North, Phillips & Mathews, 1968;

Table 1. *Fractional coordinates and isotropic vibrational parameters*

	x	y	z	U^*
Cl	0·8048 (1)	0·0134 (1)	0·5804 (1)	74 (1)
C(1)	0·7630 (2)	−0·0482 (3)	0·3990 (3)	51 (1)
C(2)	0·8503 (3)	−0·1719 (3)	0·3249 (4)	62 (1)
C(3)	0·8165 (3)	−0·2225 (3)	0·1846 (4)	69 (1)
C(4)	0·6948 (3)	−0·1503 (4)	0·1202 (5)	75 (1)
C(5)	0·6058 (3)	−0·0259 (3)	0·1931 (4)	69 (1)
C(6)	0·6398 (2)	0·0275 (3)	0·3335 (3)	53 (1)
N(1)	0·5540 (2)	0·1545 (2)	0·4090 (3)	54 (1)
N(2)	0·4377 (2)	0·2288 (2)	0·3463 (3)	51 (1)
C(7)	0·3639 (2)	0·3459 (3)	0·4254 (3)	48 (1)
C(8)	0·2317 (2)	0·4391 (3)	0·3859 (3)	44 (1)
C(9)	0·1547 (3)	0·4244 (3)	0·2453 (4)	64 (1)
N(3)	0·1842 (2)	0·5416 (2)	0·4941 (3)	52 (1)
N(4)	0·2814 (2)	0·5230 (2)	0·6114 (3)	51 (1)
C(10)	0·3941 (2)	0·4050 (3)	0·5763 (3)	52 (1)
O	0·4967 (2)	0·3578 (2)	0·6531 (3)	66 (1)
C(11)	0·2504 (2)	0·6140 (3)	0·7518 (3)	45 (1)
C(12)	0·1252 (2)	0·7200 (3)	0·7683 (4)	58 (1)
C(13)	0·0931 (3)	0·8076 (3)	0·9056 (4)	67 (1)
C(14)	0·1831 (3)	0·7929 (4)	1·0271 (4)	71 (1)
C(15)	0·3059 (3)	0·6903 (4)	1·0090 (4)	69 (1)
C(16)	0·3407 (3)	0·6005 (3)	0·8720 (4)	66 (1)

* The isotropic temperature factor is defined by $\exp(-8\pi^2 U[(\sin^2\theta)/\lambda^2] \times 10^3)$ (Cruickshank, 1956); $U(\text{Å}^2)$ is the final value of the refined isotropic displacement parameter before allowance for anisotropy.

max., min. transmission factors 0·998 and 0·586, respectively) and Lorentz–polarization to give 2773 unique reflections, all of non-zero intensity, with $-13 \le h \le 13$, $0 \le k \le 11$ and $-9 \le l \le 9$. All were used in the structure determination and refinement. Maximum $2\theta = 140·00°$. Two standard reflections were measured periodically (313 and $3\overline{1}3$). The variations in normalized intensities for 39 sets of measurements were 0·97 to 1·09 and 0·98 to 1·07, respectively; the average normalized intensities varied from 0·99 to 1·04. The density was measured by flotation.

The structure was solved using direct methods. The full-matrix least-squares refinement was based on F with a weighting function, w, such that $1/w = (\sigma^2 + 0·03F^2)$; σ was obtained from counting statistics. The atomic scattering factors used were those given in SHELX76 (Sheldrick, 1976). No corrections for anomalous dispersion. After anisotropic refinement of the heavy atoms, a difference Fourier synthesis indicated the positions of the hydrogen atoms. These in turn suggested that the molecule was the hydrazone tautomer. The hydrogen atoms were included in the refinement with the isotropic temperature factor of the appropriate atom and riding upon it at a distance of 1·05 Å. Refinement continued until the shifts were less than one-tenth the appropriate standard deviation (Mason, 1964). For the final refinement the methyl groups were freed from positional restraint. No attempt was made to refine the parameters of the other hydrogen atoms. 208 parameters in the final refinement. Final $R = 0·082$, $wR = 0·105$. The comparatively high R value is attributed to the use of all data, which is

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

Cl–C(1)	1·740 (3)	N(3)–N(4)	1·410 (3)
C(1)–C(2)	1·378 (4)	N(4)–C(10)	1·375 (3)
C(2)–C(3)	1·370 (5)	C(10)–O	1·230 (3)
C(3)–C(4)	1·371 (4)	C(10)–C(7)	1·468 (4)
C(4)–C(5)	1·384 (4)	N(4)–C(11)	1·414 (3)
C(5)–C(6)	1·387 (5)	C(11)–C(12)	1·393 (3)
C(6)–C(1)	1·391 (3)	C(12)–C(13)	1·373 (4)
C(6)–N(1)	1·397 (3)	C(13)–C(14)	1·381 (5)
N(1)–N(2)	1·318 (3)	C(14)–C(15)	1·364 (4)
N(2)–C(7)	1·307 (3)	C(15)–C(16)	1·383 (5)
C(7)–C(8)	1·441 (3)	C(16)–C(11)	1·380 (4)
C(8)–C(9)	1·484 (4)	N(1)–Cl	2·944 (2)
C(8)–N(3)	1·298 (3)	N(1)–O	2·746 (3)
		C(16)–O	2·961 (4)

Cl–C(1)–C(2)	120·1 (2)	N(3)–C(8)–C(7)	110·6 (2)
C(2)–C(1)–C(6)	121·1 (3)	C(8)–N(3)–N(4)	107·9 (2)
C(6)–C(1)–Cl	118·9 (2)	N(3)–N(4)–C(11)	118·9 (2)
C(1)–C(2)–C(3)	120·1 (3)	C(11)–N(4)–C(10)	129·1 (2)
C(2)–C(3)–C(4)	119·5 (3)	C(10)–N(4)–N(3)	111·8 (2)
C(3)–C(4)–C(5)	121·2 (3)	N(4)–C(10)–O	128·7 (3)
C(4)–C(5)–C(6)	119·7 (3)	O–C(10)–C(7)	127·4 (2)
C(5)–C(6)–N(1)	121·7 (2)	C(7)–C(10)–N(4)	103·9 (2)
N(1)–C(6)–C(1)	119·9 (3)	N(4)–C(11)–C(12)	118·8 (2)
C(1)–C(6)–C(5)	118·4 (2)	C(12)–C(11)–C(16)	119·5 (2)
C(6)–N(1)–N(2)	120·5 (2)	C(16)–C(11)–N(4)	121·8 (2)
N(1)–N(2)–C(7)	116·3 (2)	C(11)–C(12)–C(13)	119·5 (3)
N(2)–C(7)–C(8)	126·1 (3)	C(12)–C(13)–C(14)	121·0 (2)
C(8)–C(7)–C(10)	105·8 (2)	C(13)–C(14)–C(15)	119·2 (3)
C(10)–C(7)–N(2)	128·0 (2)	C(14)–C(15)–C(16)	120·9 (3)
C(7)–C(8)–C(9)	127·0 (2)	C(15)–C(16)–C(11)	119·9 (2)
C(9)–C(8)–N(3)	122·4 (2)		

considered to be methodologically more satisfactory than imposing an arbitrary cut-off (Hirshfeld & Rabinovich, 1973; Wilson, 1976, 1978). The final coordinates and isotropic temperature factors are given in Table 1.* The maximum and minimum electron densities in the final difference Fourier synthesis were 0·33 and −0·59 e Å^{-3}, respectively. Inspection of the table of observed and calculated structure factors indicated that one reflection, $\bar{2}\bar{2}1$, was affected by extinction. No correction was applied for this and its structure factor was included in the refinement.

The following programs were used: *SHELX*76 (Sheldrick, 1976) for solution of the structure, data processing, Fourier synthesis and least-squares refinements; *BONDLA* (Doherty, Stewart & Hall, 1983) for calculation of atomic distances and angles; *PARST* (Nardelli, 1982) for calculation of weighted least-squares planes of the molecule. Figs. 1 and 2 were drawn by *PLUTO* (Motherwell & Clegg, 1978).

Discussion. Bond lengths and angles are given in Table 2. Comparison of the observed bond lengths with accepted values (*International Tables for X-ray Crystallography*, 1968) confirms the difference Fourier synthesis, *i.e.* the hydrazone tautomer is the better

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and intermolecular distances <3·50 Å have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44976 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

model. Fig. 1 gives the molecular structure projected on to the plane containing the atoms C(2), C(9) and C(15).

The interatomic distances N(1)···O and N(1)···Cl suggest that there is a bifurcated hydrogen bond from N(1) to O and Cl. According to Pimental & McClellan (1960) the average distance for a hydrogen bond from nitrogen to chlorine is 3·21 Å. N–H···Cl bonds with similar lengths to the present one have been found in other pigment structures (Whitaker, 1977b, 1983a). There would appear to be another hydrogen bond, albeit weak, from C(16) to O. These hydrogen bonds inhibit rotation about neighbouring bonds and tend to hold parts of the molecule planar.

Although the molecule is almost planar, most atoms show significant deviation from this plane (Fig. 1). Both unsubstituted phenyl rings are planar within 2·1σ and the five-membered pyrazolone ring within 0·4σ, but they are inclined with respect to each other.
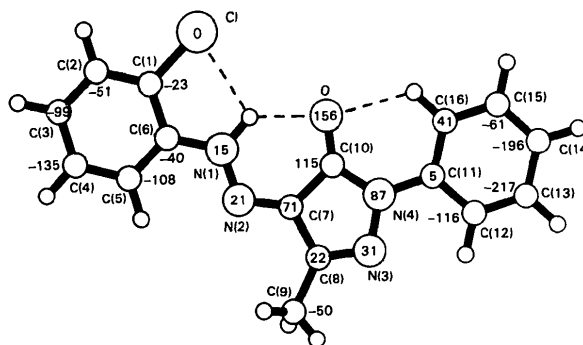

Fig. 1. Structure of the molecule projected on to the plane containing C(2), C(9) and C(15). The deviations of the atoms (in 10^{-3} Å) from the weighted least-squares plane of the molecule are also given. The errors in the atomic coordinates correspond to 0·001 Å for Cl and a mean of 0·003 Å for the other atoms. The intramolecular hydrogen bonds are indicated by broken lines.
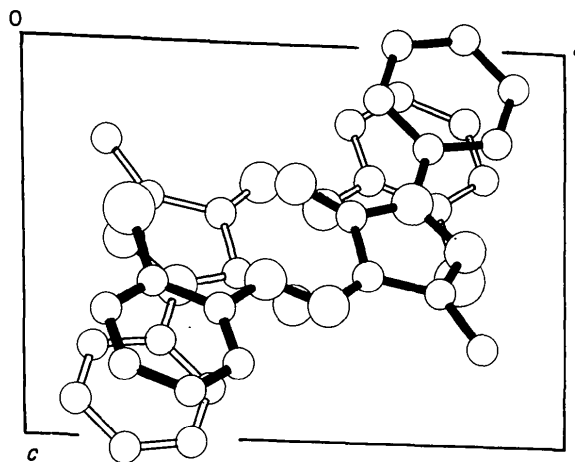

Fig. 2. The packing of CI Pigment Yellow 60 molecules in the unit cell, *b*-axis projection. The molecule at the higher level in the cell (*i.e.* that with larger *y* coordinates) is indicated by solid bonds. The molecule with open bonds has the coordinates given in Table 1.

There would appear to be no abnormal bond lengths. The molecules lie in columns parallel to the *b* axis; adjacent molecules within each column are antiparallel (Fig. 2). The normal to the weighted molecular plane is off-set 43·93 (1)° with respect to the column axis and makes an angle of 4·43 (1)° with the normal to the (22$\bar{1}$) plane. The interplanar spacing for (22$\bar{1}$) planes is 3·395 Å. A survey of intermolecular distances (excluding those involving hydrogen) reveals a C(10)···O contact of 3·139 (3) Å which is short when compared with the sum of the van der Waals radii given by Bondi (1964).

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(*E*)-1-Chloro-2-methoxy-1,2-diphenylethylene

BY A. JERRY KRESGE, JEFFERY F. SAWYER AND TAHER I. YOUSAF

Department of Chemistry, University of Toronto, 80 St George Street, Toronto, Ontario, Canada M5S 1A1

Abstract. $C_{15}H_{13}ClO$, $M_r = 244·7$, triclinic, $P\bar{1}$, $a = 7·730$ (2), $b = 8·674$ (3), $c = 9·708$ (5) Å, $\alpha = 82·81$ (3), $\beta = 79·13$ (4), $\gamma = 79·59$ (4)°, $V = 626$ Å^3, $Z = 2$, $D_x = 1·30$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0·71069$ Å, $\mu = 2·8$ cm^{-1}, $F(000) = 256$, $T = 298$ K, $R = 0·0526$ for 1512 reflections with $I > 3\sigma(I)$. The *E* stereochemistry of the molecule is established. The central C=C bond length is 1·336 (4) Å and there is a 3:1 disorder of the oxygen atom of the methoxy group. The mean planes of the two phenyl rings make angles of 43·1 and 105·0° with respect to the plane Cl(1)–C(1)–C(2) from which the atoms C(4), C(10), O(1*a*) and O(1*b*) deviate by −0·045 (3), 0·103 (3), −0·350 (6) and 0·574 (14) Å, respectively.