Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

C.I. Pigment Red 266

Chia-Hsien Chang,[a] Robert M. Christie[a] and Georgina M. Rosair[b]*

[a]School of Textiles and Design, Heriot–Watt University, Scottish Borders Campus, Galashiels TD1 3HF, Scotland, and [b]Department of Chemistry, Heriot–Watt University, Riccarton, Edinburgh EH14 4AS, Scotland
Correspondence e-mail: g.m.rosair@hw.ac.uk

Received 5 August 2003
Accepted 11 August 2003
Online 16 September 2003

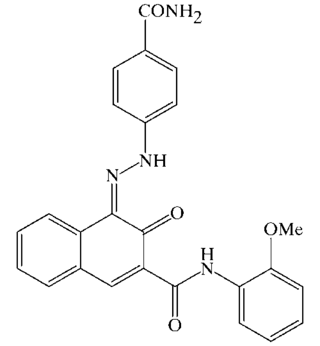
C.I. Pigment Red 266, or 4-{[4-(aminocarbonyl)phenyl]-hydrazono}-*N*-(2-methoxyphenyl)-3-oxo-3,4-dihydronaphthalene-2-carboxamide, $C_{25}H_{20}N_4O_4$, adopts the keto–hydrazone tautomeric form with significant intramolecular hydrogen bonding. The molecules pack to form layers involving an extensive network of intermolecular hydrogen bonds, in which the primary amide group plays a prominent role. The good technical performance of this pigment in application may be attributed principally to the pattern of intra- and intermolecular hydrogen bonding.

Comment

Organic pigments are insoluble colouring materials which are manufactured in a finely divided crystalline form (Christie, 2002). Their application properties are dependent on chemical structure and molecular packing in the solid state, in addition to particle size and shape distribution. Single-crystal X-ray crystallography information is vital in understanding the technical performance of pigments, including colour and fastness properties, and is an essential first step in the crystal engineering of new products for improved performance.

Naphthol azo red (or Naphthol AS) pigments constitute a group of products of industrial importance for application principally in coatings and printing inks. These products can be conveniently classified into two groups. Group 1 pigments contain a single amide group and generally provide only moderate technical performance. A number of single-crystal X-ray structures of these pigments have been reported previously (Kobelt *et al.*, 1972, 1974; Whitaker, 1977). Group 2 pigments, with additional amide or sulfonamide substituents, provide improved technical performance, yet these pigments have been less extensively investigated. In the only previous study, the X-ray crystal structure of C.I. Pigment Red 208, which contains a benzimidazolone group, has shown that the molecules are linked by a network of hydrogen bonds (Paulus & Hunger, 1980), a feature that is primarily responsible for the superior technical performance of this pigment.

C.I. Pigment Red 266, (I), is also in group 2, and investigation of the crystallographic features, notably hydrogen bonding, that contribute to its superior technical performance, such as lightfastness, solvent resistance and thermal stability, is of industrial interest. Compound (I) possesses both primary and secondary amide groups. The latter is a commonly encountered structural feature in azo pigments, yet the presence of the primary amide group is unusual in commercial organic pigments.



(I)

In common with all of the azo pigments whose crystal structures have been reported previously (Hunger, 1999), (I) exists in the keto–hydrazone tautomeric form (Fig. 1). Important bond lengths that can be highlighted in this respect are N1—N2, N2—C20 and C21—O21 (Table 1), which are similar to those reported for group 1 naphthol azo pigments [N—N = 1.32 (1)–1.336 (8) Å, C—N = 1.322 (9)–1.33 (1) Å and C—O = 1.255 (9)–1.26 (1) Å; Kobelt *et al.*, 1972, 1974].

The shortest of the hydrogen bonds found in (I) are intramolecular hydrogen bonds bifurcated at the acceptor end. This hydrogen-bonding arrangement, involving N—H and C═O groups, is commonly encountered in commercial azo pigments (Christie, 2002). Interatomic distances indicate strong hydrogen-bonding interactions between hydrazone atom H1 and keto atom O21, and between atom O21 and

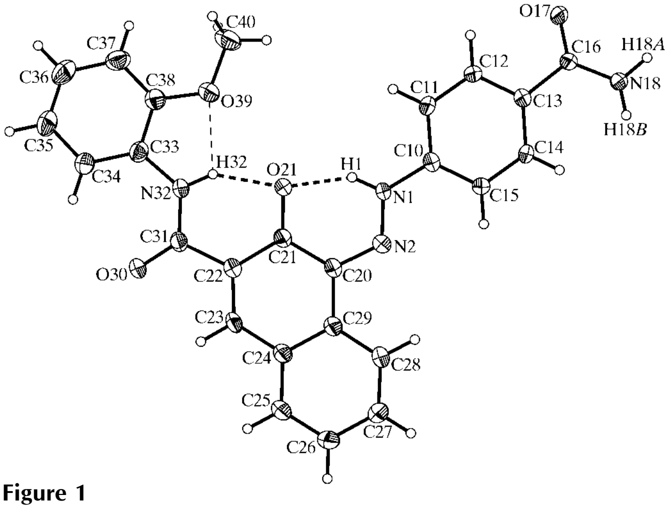


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids. Intramolecular hydrogen bonds are indicated by heavy dashed lines, with the secondary, longer, interaction indicated by a lighter dashed line.

DOI: 10.1107/S0108270103017906

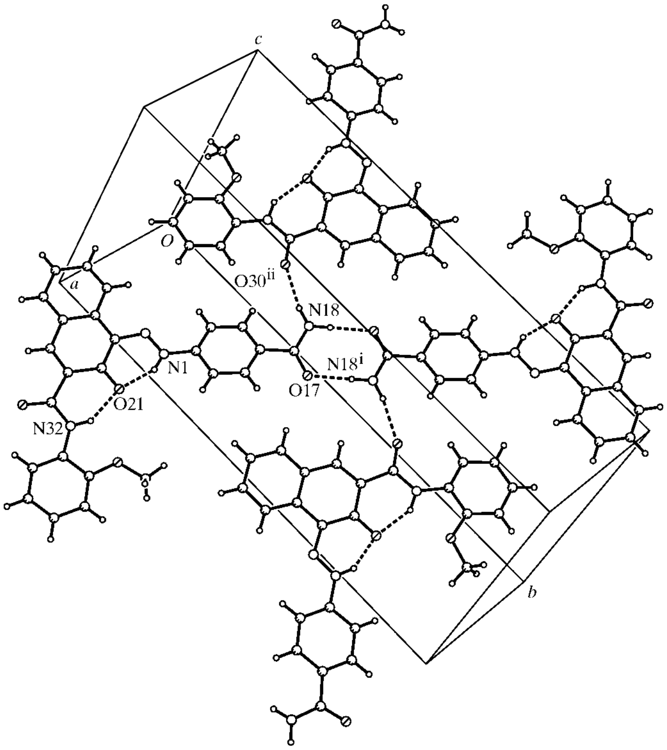


Figure 2
The primary hydrogen-bonding network in (I). The reference molecule is at $(\frac{1}{2}+x, \frac{1}{2}-y, z-\frac{1}{2})$ and the symmetry codes (i) and (ii) are $(\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z)$ and $(x-1, y, z)$, respectively.

secondary amide atom H32 (Table 2). The strong hydrogen bonds involving atom O21 probably contribute to the lengthening of the C═O bond. There is also a weaker interaction between atom H32 and methoxy atom O39. Intramolecular hydrogen bonding of this type is considered vital in determining lightfastness properties by providing electronic protection of the chromophore towards photochemical degradation.

Extensive intermolecular hydrogen bonding is also observed, with the primary amide group playing a prominent role. This functional group forms a dimeric $R_2^2(8)$ hydrogen-bonded arrangement (Etter, 1990; Etter & MacDonald, 1990), with the equivalent group in another molecule related by a centre of inversion (Table 2 and Fig. 2). The hydrogen-bonded network extends beyond the eight-membered ring *via* an N—H···O interaction involving the primary amide atoms N18/H18*B* and the secondary amide atom O30$(x-\frac{3}{2}, \frac{1}{2}-y, \frac{1}{2}+z)$. A longer C—H···O interaction (2.56 Å) links atom O17 to atom H25$(\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z)$ in the naphthol ring system, while another intralayer C—H···O interaction involves the secondary amide atom O30 and atom H14 in a different adjacent molecule (Table 2).

The pigment molecules are associated in layers as a result of an extensive two-dimensional network of intermolecular hydrogen bonds. These sheets are not parallel to any crystallographic axis but are inclined to the *c* axis at an angle of 22.95 (2)°. Weaker C—H···O and C—H···N contacts between layers can also be identified. The primary amide atoms O17 and N18 have very weak intermolecular interactions with atom H11 of a phenylhydrazone ring and with atom H12 of a phenylhydrazone ring, respectively, of molecules in the next layer (Table 2). The C16—N18···H11$(x-1, y, z)$ and C16—O17···H12$(1-x, -y, 2-z)$ angles at the acceptor atoms are 114 and 115°, respectively. Enhanced technical performance, especially solvent resistance, can be attributed primarily to the extensive intermolecular association present in (I), in contrast to the situation for group 1 products, in which the intermolecular interactions are predominantly of the van der Waals type (Whitaker, 1978).

In the solid state, the molecule of (I) deviates slightly from planarity, with the phenylhydrazone and anilide rings both twisted slightly with respect to the naphthol plane. The r.m.s. deviation from the least-squares molecular plane defined by all the non-H atoms is 0.097 Å. The angle between the two fused rings of the naphthol system is 2.63 (8)°. The phenylhydrazone (C10–C15) and anilide (C33–C38) rings form angles of 10.91 (7) and 6.67 (6)°, respectively, with the mean plane of the naphthol system (C20–C29). The primary amide group is twisted by 18.57 (14)° with respect to the phenyl ring to which it is attached, possibly in order to accommodate the dimeric hydrogen-bonding arrangement with its neighbour.

Experimental

C.I. Pigment Red 266 was synthesized by diazotization of 4-aminobenzamide, using sodium nitrite in dilute hydrochloric acid, and reaction of the resulting diazonium salt with 3-hydroxy-*N*-(2-methoxyphenyl)-2-naphthalenecarboxamide (Naphthol AS-OL), using a simultaneous aqueous azo-coupling procedure at pH 5–6 (Hoechst, 1974). Crystals suitable for X-ray analysis were obtained by slow cooling of a solution of the pigment in nitrobenzene, contained in a sealed tube, from 463 K.

Crystal data

$C_{25}H_{20}N_4O_4$
$M_r = 440.45$
Monoclinic, $P2_1/n$
$a = 7.254$ (1) Å
$b = 24.115$ (3) Å
$c = 11.565$ (2) Å
$\beta = 94.22$ (1)°
$V = 2017.6$ (5) Å^3
$Z = 4$

$D_x = 1.450$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 56 reflections
$\theta = 6.7$–30.7°
$\mu = 0.10$ mm^{-1}
$T = 160$ (2) K
Triangular plate, red
0.54 × 0.42 × 0.20 mm

Data collection

Bruker *P*4 diffractometer
ω scans
4668 measured reflections
3549 independent reflections
2761 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.026$
$\theta_{\rm max} = 25.0°$

$h = -1 \rightarrow 8$
$k = -1 \rightarrow 28$
$l = -13 \rightarrow 13$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.110$
$S = 1.01$
3549 reflections
311 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2 + 0.3084P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—N2	1.3012 (19)	O30—C31	1.2332 (19)
N1—C10	1.400 (2)	C31—N32	1.353 (2)
N2—C20	1.346 (2)	N32—C33	1.411 (2)
C16—O17	1.2388 (19)	C38—O39	1.369 (2)
C16—N18	1.334 (2)	O39—C40	1.421 (2)
C21—O21	1.268 (2)		
N2—N1—C10	122.76 (14)	O17—C16—C13	119.58 (15)
N1—N2—C20	117.75 (14)	C38—O39—C40	117.98 (15)
O17—C16—N18	122.20 (15)		
C10—N1—N2—C20	−177.33 (14)	O21—C21—C22—C31	4.1 (2)
N1—N2—C20—C21	2.2 (2)	C21—C22—C31—N32	2.7 (2)
N2—C20—C21—O21	−1.4 (2)	N32—C33—C38—O39	2.1 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O21	0.85 (2)	1.73 (2)	2.4845 (18)	147.4 (18)
N18—H18*A*···O17^{i}	0.94 (2)	1.94 (2)	2.8747 (19)	177.4 (17)
N18—H18*B*···O30^{ii}	0.90 (2)	2.11 (2)	2.9929 (19)	166.7 (18)
N32—H32···O21	0.89 (2)	1.84 (2)	2.6178 (18)	145.2 (17)
N32—H32···O39	0.89 (2)	2.155 (19)	2.5796 (18)	108.8 (15)
C11—H11···N18^{iii}	0.95	2.75	3.419 (2)	128
C12—H12···O17^{iv}	0.95	2.72	3.434 (2)	133
C14—H14···O30^{ii}	0.95	2.52	3.387 (2)	152

Symmetry codes: (i) $-x, -y, 2-z$; (ii) $x-\frac{3}{2}, \frac{1}{2}-y, \frac{1}{2}+z$; (iii) $1+x, y, z$; (iv) $1-x, -y, 2-z$.

Amide and amine H atoms were located from a difference Fourier map and their positions were refined freely. Other H-atom positions were calculated and constrained to idealized positions, with C—H distances of 0.98 (phenyl), 0.97 (methylene) and 0.96 Å (methyl). The $U_{\rm iso}$(H) values were defined as 1.2 (amino, phenyl and methylene) or 1.5 (methyl) times the $U_{\rm eq}$ values of the parent atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*.

The authors thank Dominion Colour Corporation, Toronto, Canada, for financial support, and Dr Mark Vincent and Mr Alan Gray of that organization for helpful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1174). Services for accessing these data are described at the back of the journal.

References

Bruker (1999). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.

Christie, R. M. (2002). In *The Organic and Inorganic Chemistry of Pigments*. London: Oil and Colour Chemists' Association.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Etter, M. C. & MacDonald, J. C. (1990). *Acta Cryst.* B**46**, 256–262.

Hoechst (1974). UK Patent No. 1360422.

Hunger, K. (1999). *Rev. Prog. Color.* **29**, 71–84.

Kobelt, D., Paulus, E. F. & Kunstmann, W. (1972). *Acta Cryst.* B**28**, 1319–1324.

Kobelt, D., Paulus, E. F. & Kunstmann, W. (1974). *Z. Kristallogr.* **139**, 15–32.

Paulus, E. F. & Hunger, K. (1980). *Farbe Lack*, **86**, 116–120.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Whitaker, A. (1977). *Z. Kristallogr.* **146**, 173–184.

Whitaker, A. (1978). *J. Soc. Dyers Colour.* **94**, 431–435.