

# Crystal and molecular structure of C.I. Solvent Yellow 2, 1-phenylazo-4 (N,N-dimethylamine)-phenyl

A. Whitaker<sup>1</sup>

Received May 15, 1991

The crystal structure of C.I. Solvent Yellow 2, C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>, has been determined by single crystal X-ray diffraction techniques. It crystallizes in the orthorhombic system with  $a = 6.059(2)$  Å,  $b = 7.398(1)$  Å,  $c = 27.467(4)$  Å, space group  $P2_12_12_1$ ,  $Z = 4$ . The structure has been solved by direct methods and least-squares has been completed on three dimensional data (688 reflections, Mo  $K\alpha$  radiation). The hydrogen positions have been found but only their positional parameters refined. Final residual 0.055 (all positive intensity data). The molecule exists as an azo-compound and is almost planar. The molecules are packed in columns parallel to the  $b$  axis, within each column they are packed in layers almost parallel to the (130) or ( $\bar{1}$ 30) plane depending on the column. The molecules are linked by van der Waals' forces.

## Introduction

Some years ago, with the long-term aim of relating crystal structure and color, work was published on the structure determinations of several azo-pigments involving  $\beta$ -naphthol (Grainger and McConnell, 1969; Kobelt *et al.*, 1972, 1974; Whitaker, 1977a,b, 1978a). A review (Whitaker, 1978b) 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 (Paulus, 1982; Whitaker, 1980, 1981) on other members of this group of pigments supported this view.

Interest then moved to azo-pigments involving aceto acetanilide and again a series of crystal structures were determined (Brown and Yadav, 1984; Paulus *et al.*, 1983, 1984; Whitaker, 1983a,b, 1984a,b, 1985a,b, 1986, 1987; Whitaker and Walker, 1985, 1987). The general conclusion from these was that this group of compounds should be classed as hydrazone rather than azo-pigments (Whitaker, 1988a).

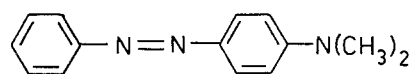
A third group of azo-colorants are those involving

pyrazolone; four crystal structures have been reported in this group (Golinski, *et al.*, 1982; Whitaker, 1988b,c, 1991). Again it is claimed that the molecules exist in the hydrazone form.

There is a common feature in all three groups of colorants, the usual azo-formula includes an hydroxyl group. However, the crystal structure determinations have shown that these compounds exist in the form of the hydrazone-ketone tautomer, the hydrogen atom having migrated from the hydroxyl to azo group.

The question then arose as to what happened if the colorant did not contain an hydroxyl group. Was the azo group stable? Or did it become a hydrazone group by the migration of an hydrogen atom from another atom; with the possibility of the molecule becoming polar? It was therefore decided to investigate colorants which do not contain a hydroxyl group.

C.I. Solvent Yellow 2 (C.I. 11020) is one such commercially available dye used in polishes, polystyrene and soap. It has the formula



Scheme 1

<sup>1</sup> Department of Physics, Brunel University, Uxbridge, Middlesex UB8 3PH, England.

## Experimental

Single crystals were obtained from the commercial dye Oil Yellow 2G by the slow cooling of a hot (65°C) saturated solution in chlorobenzene. Optical examination indicated yellow crystals, mainly plate-like, together with a few blades. Laue photographs indicated that the crystal system was orthorhombic.

A crystal of size 0.68, 0.68, 0.12 mm was used for intensity measurements. The intensity data was collected on an Enraf-Nonius CAD-4 automatic diffractometer of the National Diffractometer Service using  $\omega/2\theta$  scans and filtered molybdenum radiation. The cell dimensions were obtained by least squares refinement of the setting angles of 25 reflections while the space group was uniquely determined from systematic absences ( $h00$  absent when  $h$  is odd,  $0k0$  absent when  $k$  is odd,  $00l$  absent when  $l$  is odd). The results of these measurements are  $a = 6.059 \pm 0.002 \text{ \AA}$ ,  $b = 7.398 \pm 0.001 \text{ \AA}$ ,  $c = 27.467 \pm 0.004 \text{ \AA}$ ,  $V = 1231.3 \pm 0.5 \text{ \AA}^3$ . Space Group  $P2_12_12_1$  (No. 19). Calculated density for  $Z = 4$ ,  $1.2233 \pm 0.0005 \text{ g cm}^{-3}$ .

The intensities of 1406 reflection were collected. The intensities were corrected for the Lorentz-polarization factor but not for absorption. (The linear absorption coefficient for this compound in molybdenum radiation is  $0.41 \text{ cm}^{-1}$  and this gives a transmission factor of 0.973 along the longest length of the crystal). These were merged to give a unique set of 720 reflections with  $0 \leq h \leq 6$ ,  $0 \leq k \leq 5$  and  $0 \leq l \leq 18$ . Of these, 32 reflections were less than zero, the refinement was carried out on the remaining 688.  $R_{\text{int}}$  for ( $hkl$ ) reflections 0.022. Two standard reflections were measured periodically. The variation in the average normalized intensities from the pair varied from 0.981 to 1.009 for 23 sets. It was assumed that the change in average normalized intensities was linear between adjacent measurements. Measured intensities were corrected on this assumption.

The structure was solved by direct methods. The full-matrix least-squares refinement was based on  $F$  with a weighting function  $\omega$ , such that  $1/\omega = (\sigma^2(F) + 0.03 F^2)$ ;  $\sigma(F)$  was obtained from counting statistics. No correction was applied for anomalous dispersion.

After anisotropic refinement of the heavy atoms, a difference Fourier synthesis indicated the positions of the hydrogen atoms. These suggested that the molecule contained an azo bond, rather than an hydrazone one.

The hydrogen atoms were included in the refinement with the fixed isotropic temperature factor of the adjacent heavy atom and riding upon it at a distance of

1.00 Å. Refinements continued until the shifts were less than one-tenth of the appropriate standard deviation (Mason, 1964).

The final residual was 0.055 and the final weighted residual 0.069. The comparatively high value of these residuals is attributed to the use of all available positive intensity data, which is considered to be methodologically more satisfactory than imposing an arbitrary cut-off value (Hirshfeld and Rabinovich, 1973; Wilson, 1976, 1978). The final coordinates together with the isotropic temperature factors, are given in Table 1. The maximum and minimum densities on the final difference Fourier synthesis are  $+0.18 \text{ e \AA}^{-3}$  and  $-0.16 \text{ e \AA}^{-3}$ , respectively. Many investigators do not use all positive data but truncate the weak data at an arbitrary value,

**Table 1.** Coordinates and esd's. after anisotropic refinement, the temperature factors after isotropic refinement. The temperature factor is defined by  $\exp [(-8\pi^2 U \sin^2 \theta / \lambda^2) \times 10^{-3}]$  (Cruickshank, 1956)

Atom	$x$	$y$	$z$	$U(\text{\AA}^2)$
C(1)	0.4801(9)	0.0728(7)	0.5175(3)	[62(2)]
H(1)	0.628	0.123	0.526	62
C(2)	0.4132(11)	0.0582(9)	0.4697(3)	[73(3)]
H(2)	0.514	0.102	0.443	73
C(3)	0.2111(11)	-0.0144(10)	0.4570(3)	[79(2)]
H(3)	0.168	-0.025	0.422	79
C(4)	0.0740(10)	-0.0707(8)	0.4921(3)	[70(2)]
H(4)	-0.072	-0.125	0.483	70
C(5)	0.1322(8)	-0.0550(8)	0.5410(3)	[57(2)]
H(5)	0.027	-0.095	0.567	57
C(6)	0.3354(8)	0.0160(8)	0.5537(3)	[50(2)]
N(1)	0.3833(7)	0.0208(7)	0.6040(2)	[57(1)]
N(2)	0.5718(7)	0.0830(6)	0.6139(2)	[52(1)]
C(7)	0.6276(8)	0.0848(8)	0.6640(2)	[45(1)]
C(8)	0.4987(7)	0.0104(8)	0.7015(2)	[52(2)]
H(8)	0.354	-0.047	0.693	52
C(9)	0.5642(7)	0.0138(8)	0.7484(2)	[52(2)]
H(9)	0.468	-0.042	0.774	52
C(10)	0.7678(8)	0.0954(7)	0.7621(2)	[41(1)]
C(11)	0.8927(9)	0.1692(8)	0.7244(2)	[51(2)]
H(11)	1.036	0.230	0.732	51
C(12)	0.8258(7)	0.1618(8)	0.6772(2)	[50(2)]
H(12)	0.923	0.214	0.651	50
N(3)	0.8309(6)	0.1002(7)	0.8091(2)	[51(1)]
C(13)	0.6890(12)	0.0392(10)	0.8482(3)	[70(3)]
H(131)	0.742(10)	0.106(7)	0.883(2)	70
H(132)	0.544(10)	0.100(8)	0.841(2)	70
H(133)	0.720(13)	-0.047(8)	0.851(2)	70
C(14)	1.0393(9)	0.1788(12)	0.8224(3)	[64(2)]
H(141)	1.153(9)	0.236(7)	0.800(2)	64
H(142)	1.026(9)	0.258(9)	0.847(2)	64
H(143)	1.104(10)	0.132(9)	0.848(2)	64

often  $F = 3\sigma(F)$ . With this criterion the final residual and weighted residual were 0.048 and 0.060 respectively for the final parameters without further refinement (608 reflections in the truncated set). A table of the anisotropic temperature factors  $U_{ij}$  have been deposited together with a table of observed and calculated structure factors. There appears to be no evidence that any were affected by extinction.

The following programmes were used: SHELX 76 (Sheldrick, 1976) for data processing, solution of the structure, Fourier synthesis and least-squares refinement; BONDLA (Doherty *et al.*, 1983) for calculation of atomic distances and angles; PARST (Nardelli, 1982) for calculation of weighted least-squares planes of the molecule. Figures 1 and 2 were drawn by PLUTO.

## Discussion

The intramolecular bond lengths are given in Table 2 and the bond angles in Table 3. There would appear to be no abnormal bond lengths. Comparison of the observed bond lengths with the accepted values (Allen, *et al.*, 1987) independently confirms the difference Fourier that azo (rather than hydrazone) bonding occurs in this compound. Figure 1 gives the molecular structure projected on to the plane containing atoms C(1), C(8), and N(3).

Whereas many dyes and pigments contain intramolecular hydrogen bonds which tend to keep the molecule planar, this compound does not. In spite of this

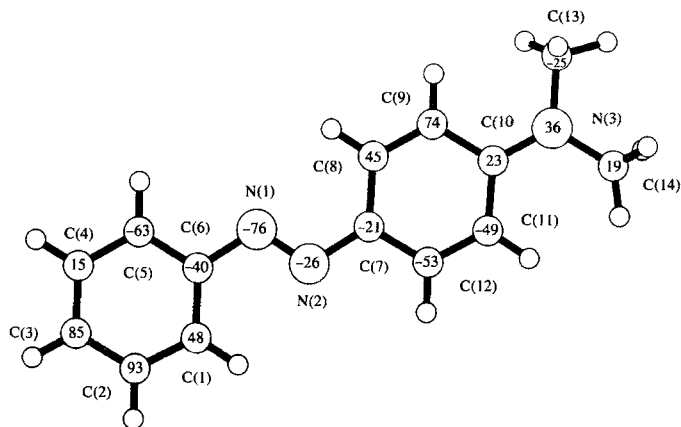
Table 2. Intramolecular atomic distance (Å)

C(1)—C(2)	1.377(11)	C(10)—C(11)	1.395(9)
C(2)—C(3)	1.383(10)	C(11)—C(12)	1.360(9)
C(3)—C(4)	1.341(10)	C(12)—C(7)	1.378(7)
C(4)—C(5)	1.393(11)	C(10)—N(3)	1.347(8)
C(5)—C(6)	1.383(7)	N(3)—C(13)	1.446(9)
C(6)—C(1)	1.390(9)	C(13)—H(131)	1.11(6)
C(6)—N(1)	1.414(9)	C(13)—H(132)	1.06(6)
N(1)—N(2)	1.261(6)	C(13)—H(133)	0.67(6)
N(2)—C(7)	1.415(9)	N(3)—C(14)	1.437(8)
C(7)—C(8)	1.405(9)	C(14)—H(141)	1.01(5)
C(8)—C(9)	1.350(9)	C(14)—H(142)	0.91(7)
C(9)—C(10)	1.424(7)	C(14)—H(143)	0.89(6)

lack of intramolecular hydrogen bonding, the molecular is almost planar and the equation of the plane through the heavy atoms (by weighted least-squares fit) is  $0.4275(14)X - 0.8993(7)Y - 0.0922(7)Z = -0.6000(10)$ , where  $X$ ,  $Y$ , and  $Z$  are parallel to the axes of the unit cell. The derivations of the atoms from this plane are given in Figure 1; the maximum deviation is 0.093 Å for C(2). Although the deviations are small when measured in Å; virtually all are significant (greater than  $3\sigma$ ), when the standard deviation,  $\sigma$ , of the atomic coordinates are taken into account. What is more, the deviations are not at random. Both the phenyl groups are planar with  $2.2\sigma$  but they are inclined at an angle of  $6.1(2)^\circ$  with respect to each other, while the dimethylamine group is inclined at an angle of  $5.3(5)^\circ$  with respect to the adjacent phenyl. It is these angles of incli-

Table 3. Intramolecular bond angle ( $^\circ$ )

C(2)—C(1)—C(6)	118.1(0.6)	C(12)—C(11)—C(10)	122.1(0.5)
C(3)—C(2)—C(1)	122.2(0.7)	C(7)—C(12)—C(11)	121.8(0.6)
C(4)—C(3)—C(2)	119.1(0.7)	C(10)—N(3)—C(13)	122.2(0.5)
C(5)—C(4)—C(3)	120.8(0.6)	C(13)—N(3)—C(14)	117.4(0.6)
C(6)—C(5)—C(4)	119.9(0.6)	C(14)—N(3)—C(10)	120.2(0.5)
C(5)—C(6)—N(1)	116.0(0.6)	N(3)—C(13)—H(131)	109(3)
N(1)—C(6)—C(1)	124.2(0.5)	N(3)—C(13)—H(132)	105(3)
C(1)—C(6)—C(5)	119.8(0.6)	N(3)—C(13)—H(133)	103(6)
C(6)—N(1)—N(2)	114.0(0.5)	H(131)—C(13)—H(132)	103(4)
N(1)—N(2)—C(7)	115.5(0.5)	H(131)—C(13)—H(133)	104(7)
N(2)—C(7)—C(8)	125.1(0.5)	H(132)—C(13)—H(133)	132(7)
C(8)—C(7)—C(12)	117.0(0.6)	N(3)—C(14)—H(141)	128(3)
C(12)—C(7)—N(2)	117.9(0.6)	N(3)—C(14)—H(142)	112(3)
C(9)—C(8)—C(7)	122.0(0.5)	N(3)—C(14)—H(143)	116(4)
C(10)—C(9)—C(8)	121.0(0.6)	H(141)—C(14)—H(142)	104(5)
C(9)—C(10)—N(3)	120.7(0.5)	H(141)—C(14)—H(143)	110(5)
N(3)—C(10)—C(11)	123.2(0.5)	H(142)—C(14)—H(143)	71(6)
C(11)—C(10)—C(9)	116.1(0.6)		



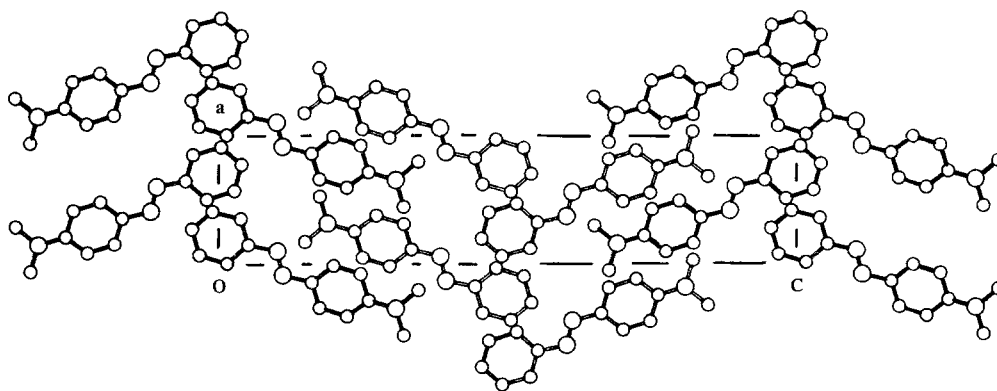
**Fig. 1.** Structure of the molecule projected on to the plane containing C(1), C(8), and N(3). The deviations of the atoms (in  $10^{-3}$  Å) from the weighted least-squares plane of the molecule are given. The error in the atomic coordinates correspond to a mean of 0.006 Å.

nation between adjacent parts of the molecule which cause significantly large deviations from the least squares fit through the molecule, rather than a random distribution of deviations.

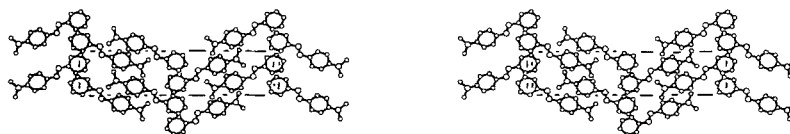
The molecules lie in columns parallel to the *b* axis (Fig 2), the molecule is not perpendicular to the column axis, the normal to the molecular plane is off-set  $25.93(7)^\circ$  with respect to it but only  $6.22(5)^\circ$  off-set

from the (130) plane. This explains the large structure factor of this plane.

Calculations of intermolecular distances indicated that heavy atoms are not involved in any less than 3.50 Å, and thus the intermolecular contacts must be due to van der Waals' forces. There are no intermolecular hydrogen bonds as found in some other colorants (Whitaker, 1983a, 1987; Whitaker and Walker, 1987).



**Fig. 2a.** The packing of C.I. Solvent Yellow 2 molecules in the cell, *b* axis projection, molecules whose centers of mass are at  $y \geq 0.5$  are indicated by solid bonds.



**Fig. 2b.** A stereoscopic pair showing the packing of C.I. Solvent Yellow 2 molecules in the unit cell, *b* axis projection.

Unlike all previous structure determinations of so-called 'azo-colorants,' where it has been shown that the chromophore has been an hydrozono rather than an azo group, in this case the chromophore is an azo group.

### Acknowledgments

The author would like to thank Professor M. Hursthouse, Dr. M. Motevalli, and the Science and Engineering Research Council National X-ray Crystallographic Service for collecting the data. The dye was kindly provided by Amritlal Chemaux Ltd.

### References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G., and Taylor, R. (1987) *J. Chem. Soc. Perkin Trans. II*, S1-S19.
- Brown, C. J., and Yadav, H. R. (1984) *Acta Crystallogr.* **C40**, 564-566.
- Cruickshank, D. W. J. (1956) *Acta Crystallogr.* **9**, 747-753.
- Doherty, R. M., Stewart, J. M., and Hall, S. R. (1983) BONDLA. Calculation of Bond Lengths and Angles. A subroutine of XTAL system of crystallographic programs. Editors J. M. Stewart and S. R. Hall, University of Maryland, U.S.A.
- Golinski, B., Reck, G., and Kutschabsky, L. (1982) *Z. Kristallogr.* **158**, 271-278.
- Grainger, C. T., and McConnell, J. F. (1969) *Acta Crystallogr.* **B25**, 1962-1970.
- Hirshfeld, F. L., and Rabinovich, D. (1973) *Acta Crystallogr.* **A29**, 510-513.
- Kobelt, D., Paulus, E. F., and Kunstmann, W. (1972) *Acta Crystallogr.* **B28**, 1319-1324.
- Kobelt, D., Paulus, E. F., and Kunstmann, W. (1974) *Z. Kristallogr.* **139**, 15-22.
- Mason, R. (1964) *Acta Crystallogr.* **17**, 547-555.
- Nardelli, M. (1982) PARST. A system of computer routines for calculating molecular parameters from the results of crystal structure analysis. University of Parma, Italy.
- Paulus, E. F. (1982) *Z. Kristallogr.* **160**, 235-243.
- Paulus, E. F. (1984) *Z. Kristallogr.* **167**, 65-72.
- Paulus, E. F., Rieper, W., and Wagner, D. (1983) *Z. Kristallogr.* **165**, 137-149.
- Sheldrick, G. M. (1976) SHELX 76. Program for Crystal Structure Determination, University of Cambridge, England.
- Whitaker, A. (1977a) *Z. Kristallogr.* **145**, 271-288.
- Whitaker, A. (1977b) *Z. Kristallogr.* **146**, 173-184.
- Whitaker, A. (1978a) *Z. Kristallogr.* **147**, 99-112.
- Whitaker, A. (1978b) *J. Soc. Dyers Color.* **94**, 431-435.
- Whitaker, A. (1980) *Z. Kristallogr.* **152**, 227-238.
- Whitaker, A. (1981) *Z. Kristallogr.* **156**, 125-138.
- Whitaker, A. (1983a) *Z. Kristallogr.* **163**, 19-30.
- Whitaker, A. (1983b) *Z. Kristallogr.* **163**, 139-149.
- Whitaker, A. (1984a) *Z. Kristallogr.* **166**, 177-188.
- Whitaker, A. (1984b) *Z. Kristallogr.* **167**, 225-233.
- Whitaker, A. (1985a) *Z. Kristallogr.* **170**, 213-223.
- Whitaker, A. (1985b) *Z. Kristallogr.* **171**, 17-22.
- Whitaker, A. (1986) *Acta Crystallogr.* **C42**, 1566-1569.
- Whitaker, A. (1987) *Acta Crystallogr.* **C43**, 2141-2144.
- Whitaker, A. (1988a) *J. Soc. Dyers Color.* **104**, 294-300.
- Whitaker, A. (1988b) *Acta Crystallogr.* **C44**, 1587-1590.
- Whitaker, A. (1988c) *Acta Crystallogr.* **C44**, 1767-1770.
- Whitaker, A. (1991) *J. Cryst. Spec. Res.* **21**, 463-469.
- Whitaker, A., and Walker, N. (1985) *Z. Kristallogr.* **171**, 7-15.
- Whitaker, A., and Walker, N. P. C. (1987) *Acta Crystallogr.* **C43**, 2137-2141.
- Wilson, A. J. C. (1976) *Acta Crystallogr.* **A32**, 994-996.
- Wilson, A. J. C. (1978) *Acta Crystallogr.* **A34**, 474-475.

Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK as supplementary publication No. 60767 (7 pages).