

Two azo pigments based on  $\beta$ -naphthol

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Received 15 May 2008

Accepted 24 July 2008

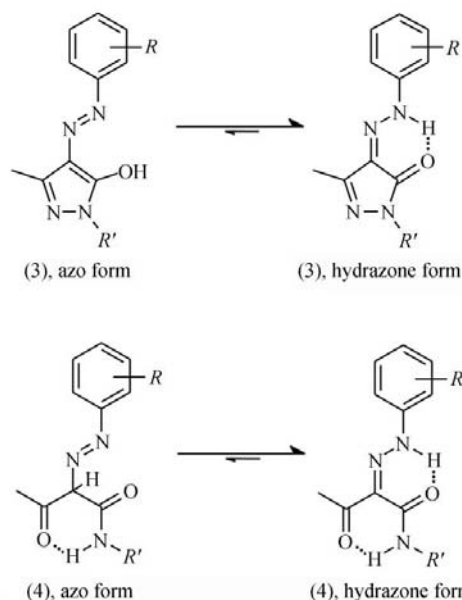
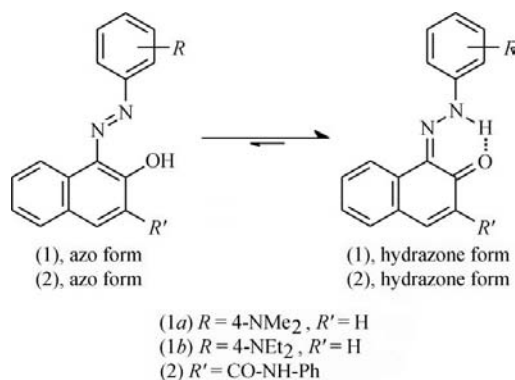
Online 9 August 2008

There has been much discussion in the literature of the azo-hydrazone tautomerism of pigments. All commercial azo pigments with  $\beta$ -naphthol as the coupling compound adopt the hydrazone tautomeric form (Ph—NH—N=C) in the solid state. In contrast, the red pigments 1-[4-(dimethylamino)phenyldiazenyl]-2-naphthol, C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O, (1*a*), and 1-[4-(diethylamino)phenyldiazenyl]-2-naphthol, C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O, (1*b*), have been reported to be azo tautomers or a mixture of azo and hydrazone tautomers in the solid state. To prove these observations, both compounds were synthesized, recrystallized and their crystal structures redetermined by single-crystal structure analysis. Difference electron-density maps show that the H atoms of the hydroxyl groups are indeed bonded to the O atoms. Nevertheless, a small amount of the hydrazone form seems to be present. Hence, the compounds are close to being 'real' azo compounds. Compound (1*a*) crystallizes with a herring-bone structure and compound (1*b*) forms a rare double herring-bone structure.

## Comment

Azo pigments are widely used for the colouration of coatings, plastics and printing inks, with an annual sales volume of more than one billion Euros (Herbst & Hunger, 2004). In the literature, most azo pigments are drawn with an N=N double bond (1-azo to 4-azo, see scheme). However, all commercial pigments based on  $\beta$ -naphthol adopt the hydrazone tautomeric form in the solid state (1-hydrazone). The same holds true for pigments with naphthol-AS, (2), pyrazolone, (3) and acetoacetanilide, (4), groups, as proven by many X-ray structure determinations of  $\beta$ -naphthol pigments (Guggenberger & Teufer, 1975; Whitaker *et al.*, 1978; Salmen *et al.*, 1988; Olivieri *et al.*, 1989; Diamantis *et al.*, 1992; Gilli *et al.*, 2002), naphthol-AS pigments (Kobelt *et al.*, 1972, 1974; Paulus *et al.*, 1982), pyrazolone pigments (Whitaker, 1995) and acetoacetanilide pigments (Paulus *et al.*, 1983; Gridunova *et al.*, 1991; Barrow *et al.*, 2002, 2003). Consequently, all these pigments should not be called 'azo pigments' but 'hydrazone pigments'.

The preference for the hydrazone tautomeric form can be explained by the fact that generally a C=N double bond is energetically more stable than an N=N double bond. In the case of  $\beta$ -naphthol and naphthol-AS pigments, the formation of the hydrazone tautomer leads to a partial loss of aromaticity in the naphthalene moiety; this does not have a major impact on the energy. For acetoacetanilide (4), the hydrazone form is additionally stabilized by the enhanced conjugation of the  $\pi$ -systems; furthermore, planar molecules can generally be packed more densely in the crystalline state, leading to higher lattice energies.



In solution, azo and hydrazone tautomers exist in an equilibrium depending on temperature, solvent and substitution pattern. The equilibrium in solution has been studied by UV-visible (Traven *et al.*, 1980; Antonov *et al.*, 1995; Antonov & Stoyanov, 1995) and NMR spectroscopy (Chippendale *et al.*, 1999; Lycka *et al.*, 2000; Birkett *et al.*, 2000; Machacek *et al.*, 2000; Alarcon *et al.*, 2004). Solid-state NMR investigations have also been carried out (Chippendale *et al.*, 1981; Olivieri *et al.*, 1989; McGeorge *et al.*, 1996, 1998). Quantum mechanical calculations have been performed (Kuder, 1972; Gilli *et al.*, 2005; Hihara *et al.*, 2003; Alarcon *et al.*, 2004). A review with 100 references is given by Mustroph (1987).

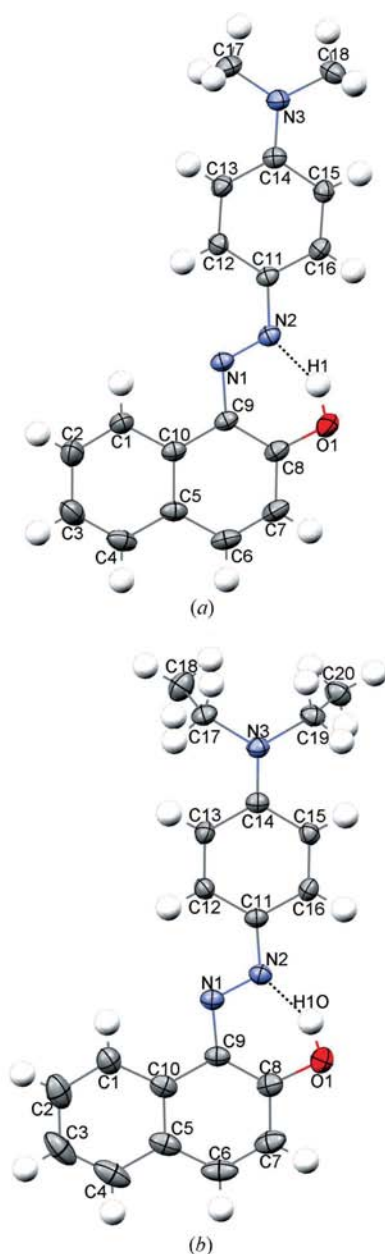
The crystal structure of 1-[4-(diethylamino)phenyl-diazenyl]-2-naphthol, (*1b*), has been determined by single-crystal X-ray analysis (Traven *et al.*, 1985). From the N—N, C—N and C—O bond lengths, the authors concluded that the compound exists 'in a form intermediate between the boundary structures' of the azo and hydrazone tautomeric forms. The X-ray structure determination of the dimethyl-amino derivative, (*1a*), in the range 100–295 K (Gilli *et al.*, 2005) showed that the H atom of the hydroxyl group is disordered over two positions with a prevalence of the azo tautomer. The ratio of occupancies of the H atom in the O—H *versus* the N—H form was determined to be 79 (1):21 (1).

Compounds (*1a*) and (*1b*) are not used commercially because their pigmentary properties, especially their consid-

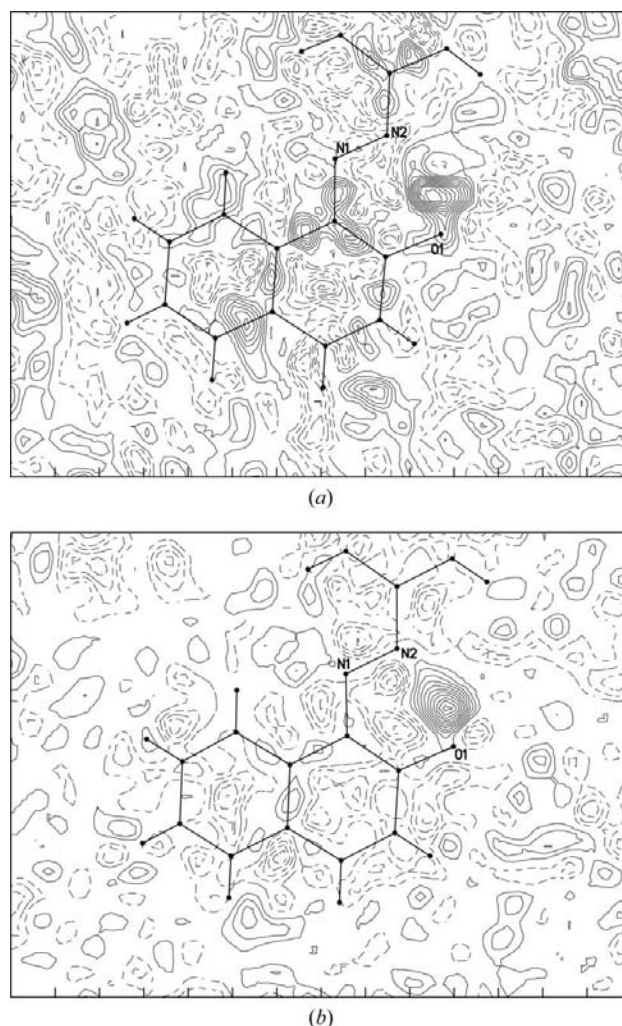
erable solubilities, do not fit the requirements for an industrial organic pigment.

We redetermined the crystal structures of (*1a*) and (*1b*) by single-crystal X-ray analysis and found that both compounds adopt the azo tautomeric form (see Fig. 1); however, in the difference electron-density plots there is still a tiny electron density at the positions of the N—H hydrogens, indicating a very small amount of the hydrazone tautomer (see Fig. 2). In both compounds, an intramolecular N···H—O (or N—H···O, respectively) hydrogen bond is formed.

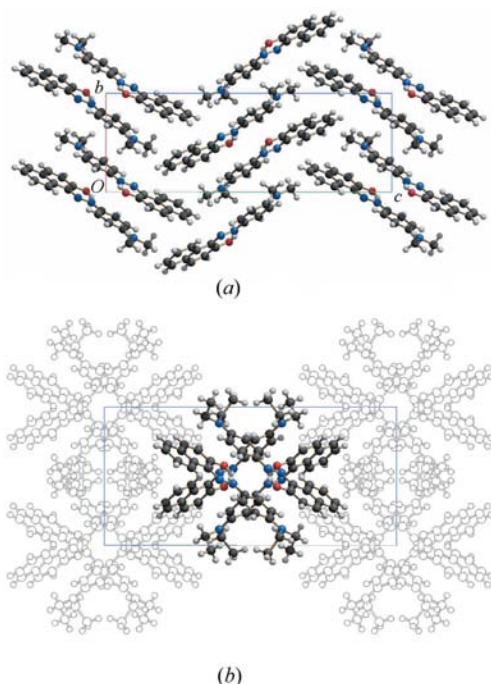
The crystal structures of (*1a*) and (*1b*) are not isotypic. Compound (*1a*) crystallizes in the space group  $P2_1/n$  with four molecules per unit cell. The molecules are essentially planar and are packed in columns in the [010] direction; within the columns, neighbouring molecules are stacked antiparallel and linked by inversion centres (see Fig. 2*a*). Each column is connected to two opposite neighbouring columns by van der Waals interactions, resulting in a sheet in the (001) direction. The sheets themselves are also arranged antiparallel, resulting in the molecules forming a herring-bone pattern. In compound



**Figure 1**  
Ellipsoid plots of (*a*) compound (*1a*) and (*b*) compound (*1b*). Ellipsoids are drawn at the 50% probability level.



**Figure 2**  
Difference electron-density maps of (*a*) compound (*1a*) and (*b*) compound (*1b*). The positions of the H atoms of the hydroxyl groups are clearly visible.



**Figure 3**  
 (a) The packing of (1a) viewed in the [100] direction. (b) The packing of (1b) viewed in the [001] direction; two pairs of molecules are highlighted (SCHAKAL99; Keller, 1999).

(1b), the molecules are planar except for the methyl groups of the diethylamino fragment which stick out of the plane by nearly  $90^\circ$ . The unit cell of (1b) contains eight molecules. The characteristic features are pairs of antiparallel molecules, with the ethyl groups pointing outwards (see Fig. 2b). There is an inversion centre between the molecules. These pairs of molecules form columns in the [001] direction, with neighbouring pairs being rotated by about  $90^\circ$ .

Kelemen *et al.* (1982) examined more than 30 compounds in an investigation of azo-hydrazone tautomerism and postulated that in a real azo compound the  $\text{N}=\text{N}$  double bond should have a length of 1.20–1.28 Å. Furthermore, the bond length of  $\text{N}-\text{N}$  single bonds, as in hydrazone tautomers, should be more than 1.4 Å. According to Harada *et al.* (1997), in nondisordered azobenzenes the  $\text{N}=\text{N}$  double bond has a length of 1.26–1.27 Å. For compounds (1a) and (1b), we found values of 1.282 (2) and 1.288 (2) Å, respectively, which are slightly larger than the value for an  $\text{N}=\text{N}$  double bond. For the  $\text{C}-\text{N}$  bond, a similar effect is observed. This is another indication that the compounds (1a) and (1b) are mainly, but not exclusively, in the azo tautomeric form, *i.e.* they are close to being ‘real’ azo pigments.

## Experimental

For the synthesis of (1a), 4-(dimethylamino)aniline was diazotized with  $\text{NaNO}_2$  in aqueous  $\text{HCl}$  and coupled with  $\beta$ -naphthol under basic conditions (Becker *et al.*, 2001). A red powder of (1a) was obtained. IR (KBr): 3049 (w), 2966 (w), 2925 (w), 2894 (w), 2866 (w), 2358 (w), 2341 (w), 1990 (w), 1890 (w), 1683 (w), 1652 (w), 1596 (s), 1558 (m), 1515 (m), 1506 (w), 1467 (w), 1402 (s), 1375 (m), 1352 (w), 1344 (w), 1313 (w), 1272 (m), 1245 (m), 1193 (w), 1164 (m), 1153 (m),

1135 (w), 1080 (s), 1010 (m), 977 (m), 958 (w), 918 (w), 864 (w), 813 (s), 783 (w), 750 (s), 729 (w), 676 (w), 669 (w), 632 (w), 565 (w), 534 (w), 511 (w), 459 (w), 447 (w), 414 (w);  $^1\text{H}$  NMR (250 MHz, DMSO, 298 K, TMS):  $\delta$  3.09 (s, 6H, H17A–C, H18A–C), 6.90 (dm, 2H, H13, H15,  $^3J = 9.3$  Hz), 7.21 (d, 1H, H7,  $^3J = 9.25$  Hz), 7.47 (ddd, 1H, H3,  $^3J_1 = 8.0$ ,  $^3J_2 = 6.9$ ,  $^3J_3 = 1.2$  Hz), 7.64 (ddd, 1H, H2,  $^3J_1 = 8.4$ ,  $^3J_2 = 6.9$ ,  $^3J_3 = 1.3$  Hz), 7.91 (m, 4H, H4, H6, H12, H16), 8.77 (d, 1H, H1A,  $^3J = 8.61$  Hz), 14.9 (s, 1H, H1); the correlations were proven by COSY (correlation spectroscopy) experiments. Compound (1a) was dissolved in boiling benzene and cooled to room temperature. The solvent was evaporated slowly at this temperature. Crystals in the form of red needles up to  $2 \times 0.32 \times 0.25$  mm were obtained.

The synthesis of (1b) was as described for (1a). A red powder of (1b) was obtained. IR (KBr): 3074 (w), 3049 (w), 2966 (m), 2925 (w), 2894 (w), 2866 (w), 2671 (w), 2611 (w), 2360 (w), 1596 (s), 1554 (w), 1515 (m), 1508 (w), 1483 (w), 1467 (m), 1456 (w), 1446 (w), 1402 (s), 1375 (s), 1352 (m), 1346 (w), 1313 (m), 1274 (s), 1247 (s), 1193 (m), 1166 (s), 1153 (m), 1135 (w), 1080 (s), 1010 (s), 977 (m), 958 (w), 918 (w), 864 (w), 813 (s), 761 (w), 750 (s), 729 (w), 676 (w), 632 (s), 565 (m), 536 (w), 520 (m), 459 (m), 447 (w), 414 (m);  $^1\text{H}$  NMR (250 MHz, DMSO, 298 K, TMS):  $\delta$  1.18 (t, 6H, H18A–C, H20A–C,  $^3J = 7$  Hz), 3.49 (q, 4H, H17A/B, H19A/B,  $^3J = 6.81$  Hz), 6.87 (d, 2H, H13, H15,  $^3J = 8.92$ ), 7.19 (d, 1H, H7,  $^3J = 8.7$  Hz), 7.47 (ddd, 1H, H3,  $^3J_1 = 8.1$ ,  $^3J_2 = 6.9$ ,  $^3J_3 = 1.2$  Hz), 7.64 (ddd, 1H, H2,  $^3J_1 = 8.3$ ,  $^3J_2 = 6.8$ ,  $^3J_3 = 1.3$  Hz), 7.91 (m, 4H, H4, H6, H12, H16), 8.77 (d, 1H, H1,  $^3J = 8.34$  Hz), 14.88 (s, 1H, H1O); the correlations were proven by COSY experiments. Compound (1b) was dissolved in boiling acetone and cooled to room temperature. The solvent was evaporated slowly at this temperature. Crystals in the form of red needles up to  $0.2 \times 0.4 \times 0.2$  mm were obtained.

## Compound (1a)

### Crystal data

|                                                |                                   |
|------------------------------------------------|-----------------------------------|
| $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}$ | $V = 1484.4$ (2) Å <sup>3</sup>   |
| $M_r = 291.35$                                 | $Z = 4$                           |
| Monoclinic, $P2_1/n$                           | Mo $K\alpha$ radiation            |
| $a = 7.6443$ (6) Å                             | $\mu = 0.08$ mm <sup>-1</sup>     |
| $b = 8.0127$ (6) Å                             | $T = 173$ (2) K                   |
| $c = 24.512$ (2) Å                             | $0.32 \times 0.14 \times 0.13$ mm |
| $\beta = 98.640$ (6)°                          |                                   |

### Data collection

|                                       |                                        |
|---------------------------------------|----------------------------------------|
| Stoe IPDSII two-circle diffractometer | 4153 independent reflections           |
| 25765 measured reflections            | 2762 reflections with $I > 2\sigma(I)$ |
|                                       | $R_{\text{int}} = 0.082$               |

### Refinement

|                                 |                                                                        |
|---------------------------------|------------------------------------------------------------------------|
| $R[F^2 > 2\sigma(F^2)] = 0.058$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.138$               |                                                                        |
| $S = 1.01$                      | $\Delta\rho_{\text{max}} = 0.28$ e Å <sup>-3</sup>                     |
| 4153 reflections                | $\Delta\rho_{\text{min}} = -0.21$ e Å <sup>-3</sup>                    |
| 205 parameters                  |                                                                        |

## Compound (1b)

### Crystal data

|                                                |                                   |
|------------------------------------------------|-----------------------------------|
| $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}$ | $V = 3367.3$ (7) Å <sup>3</sup>   |
| $M_r = 319.40$                                 | $Z = 8$                           |
| Monoclinic, $C2/c$                             | Mo $K\alpha$ radiation            |
| $a = 24.813$ (3) Å                             | $\mu = 0.08$ mm <sup>-1</sup>     |
| $b = 10.7144$ (10) Å                           | $T = 173$ (2) K                   |
| $c = 13.8806$ (19) Å                           | $0.24 \times 0.13 \times 0.12$ mm |
| $\beta = 114.150$ (9)°                         |                                   |

## Data collection

Stoe IPDSII two-circle  
diffractometer  
8777 measured reflections

3140 independent reflections  
2205 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.048$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.113$   
 $S = 0.97$   
3140 reflections  
221 parameters

H atoms treated by a mixture of  
independent and constrained  
refinement  
 $\Delta\rho_{\text{max}} = 0.12 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °) for (1a).

| $D-H \cdots A$    | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|-------------------|----------|--------------|--------------|----------------|
| O1—H1 $\cdots$ N2 | 1.00 (3) | 1.64 (3)     | 2.5429 (17)  | 148 (3)        |

Table 2

Hydrogen-bond geometry (Å, °) for (1b).

| $D-H \cdots A$     | $D-H$    | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|--------------------|----------|--------------|--------------|----------------|
| O1—H1O $\cdots$ N2 | 1.00 (3) | 1.64 (3)     | 2.5510 (19)  | 149 (2)        |

For both compounds, all H atoms were located in difference maps, but those bonded to C atoms were refined with fixed individual displacement parameters [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ ], using a riding model with aromatic, methyl and methylene C—H distances of 0.95, 0.98 and 0.99 Å, respectively. The methyl groups in (1a) were allowed to rotate but not to tip. The hydroxyl H atoms were refined isotropically.

For both compounds, data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2008).

The authors thank Professor Dr Heinz Langhals (Ludwig-Maximilian-University, Munich, Germany) for scientific discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3091). Services for accessing these data are described at the back of the journal.

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