

Monothioindigo, determined by microcrystal structure analysis

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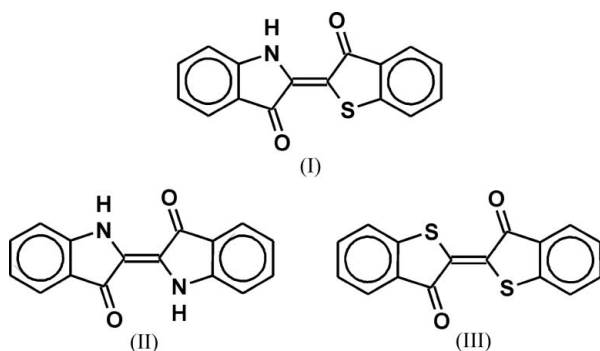
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Indigo and thioindigo pigments are used for a wide range of applications. The crystal structure of the mixed compound monothioindigo [systematic name: (*E*)-2-(3-oxo-2,3-dihydro-1-benzothiophen-2-ylidene)-2,3-dihydro-1*H*-indol-3-one], C₁₆H₉NO₂S, has been determined by microcrystal structure analysis from a crystal with a size of just 1 × 2 × 10 μm. The crystal structure of monothioindigo resembles those of indigo and thioindigo. The molecules show orientational disorder, with site-occupation factors of 0.962 (2) and 0.038 (2) for the major and minor disorder components, respectively. The indigo fragment donates an intermolecular hydrogen bond, leading to a criss-cross arrangement of molecules similar to that in indigo, whereas the thioindigo fragment exhibits only van der Waals interactions and molecular stacking, similar to that in thioindigo.

Comment

Indigo pigments are the most important vat pigments. Indigo, also known as Pigment Blue 66 and referred to hereinafter as (II) (Schmidt, 1997; Zollinger, 2003; Herbst & Hunger, 2004), has been known since ancient times and is nowadays the most frequently used natural organic pigment. The development



of the technical synthesis of (II) (Baeyer & Emmerling, 1870; Baeyer, 1880; Baeyer & Drewsen, 1882; Heumann, 1890*a,b*)

was one of the major inventions in the field of colorants in the nineteenth century. The molecular structure was determined in 1883 (Baeyer & Drewsen, 1883) and finally confirmed by X-ray crystal structure analysis in 1928 (Reis & Schneider, 1928). Replacement of the two NH groups by S atoms leads to thioindigo pigments (Formanek, 1928; Sadler, 1956; Sadler & Warren, 1956; Herbst & Hunger, 2004), *e.g.* Pigment Red 88, Pigment Red 181 and Vat Red 41, referred to hereinafter as (III). Thioindigo pigments are used for special-purpose applications, such as in cosmetics, for the coloration of rigid PVC or polystyrene, and in industrial coatings. Monothioindigo [systematic name: (*E*)-2-(3-oxo-2,3-dihydro-1-benzothiophen-2-ylidene)-2,3-dihydro-1*H*-indol-3-one], (I), has been known since 1905 (Gesellschaft für chemische Industrie in Basel, 1905, 1906). Originally, the compound was described as ‘gemischter schwefel- und stickstoffhaltiger Farbstoff der Thioindigoreihe’ (Rosenberg, 1909), but later it was included in the class of asymmetrical thioindigo dyes (Formanek, 1928). Compound (I) is synthesized from condensation of salicylthioacetic acid with isatinilide (see reaction scheme).

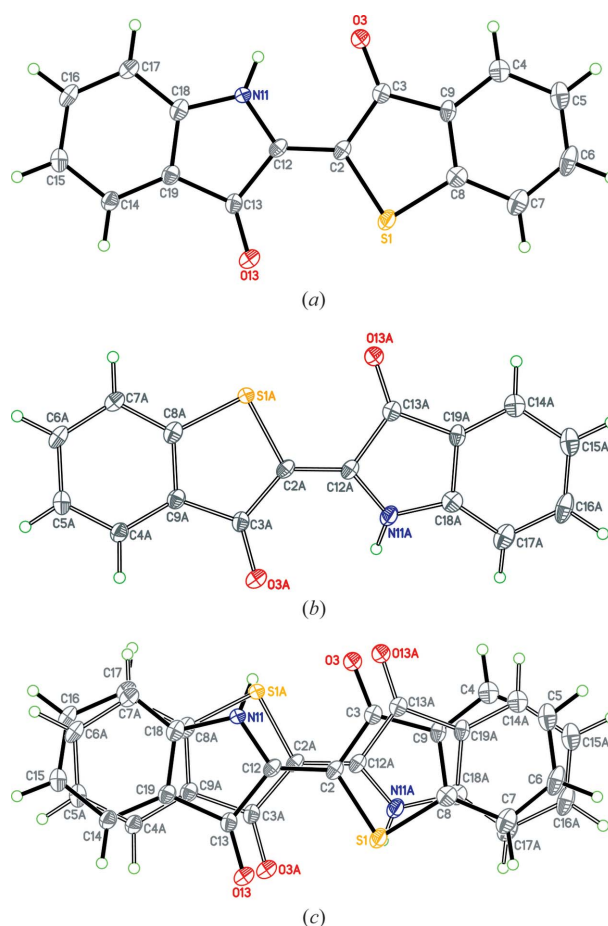


Figure 1
Perspective views of (a) the major orientation, (b) the minor orientation and (c) both orientations of (I), showing the atom-numbering scheme in each case. The major orientation is shown with full bonds and the minor orientation with open bonds. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

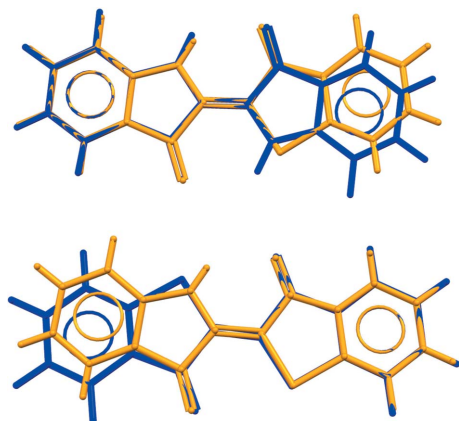
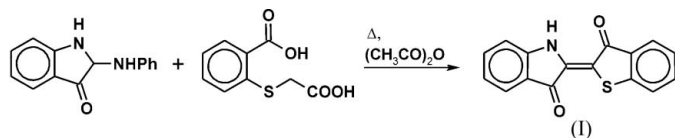


Figure 2
Comparison of the molecular structure of (I) (light shading; orange in the electronic version of the paper) with those of (II) (dark shading, top; blue) and (III) (dark shading, bottom; blue). For (I), only the major occupancy components are shown.

Compound (I) shows a reddish violet colour, which is between the colours of (II) (blue) and (III) (red). The absorption maximum of (I) in solution is at 581.4 nm (Schuster, 1928) and its lifetime in the excited state (in acetone) is about 67 (± 5) ps (Lill *et al.*, 1980). In the vat, *i.e.* in reduced form, it shows a yellow colour. Compound (I) was industrially produced by the Gesellschaft für chemische



Industrie in Basel (CIBA) under the brand names Ciba Violet A and Küpenblau, and the 5-monobromo derivative was sold as Ciba Grau (Farbwerke Höchst, 1911; Formanek, 1928). For indigo and thioindigo derivatives, a series of crystal

structures have been determined and are included in the Cambridge Structural Database (CSD; Allen, 2002; CSD refcodes: DBRING, DCINDG, DMINDG, INDIGO, KIGZOQ, KIGZUW, OXINGO, OXTIND, SEINDI, SINDIG). We present here the first crystal structure determination of a monothioindigo compound, (I). The crystal structure was determined by microcrystal structure analysis using synchrotron radiation. The crystals obtained were very small. The diffraction measurements were performed at the SLS beamline PXI (X06SA, Villigen, Switzerland). A small crystal of (I) with a size of only $1 \times 2 \times 10 \mu\text{m}$ was glued on the top of a tiny glass fibre using a microscope equipped with a micromanipulator. The beam size at the sample position was as small as $10 \times 50 \mu\text{m}$ (vertical \times horizontal). Further details are given in the *Experimental* section. The molecules are disordered over two orientations (Fig. 1).

The molecules of (I) are essentially planar. The geometries of the indoxyl and thioindoxyl fragments, *i.e.* of the two halves of the molecule of (I), are almost identical to those of (II) and (III), respectively (Fig. 2). Due to the lack of inversion symmetry in the molecule, it is slightly bent in-plane (Fig. 1). The S atom requires more space than the NH group, leading to an in-plane bending of about 14° . The N–H group forms a bifurcated hydrogen bond; an intramolecular hydrogen bond to the neighbouring O atom, and an intermolecular hydrogen bond to the carbonyl group of a neighbouring molecule (Fig. 3*b*), as in (II) (Fig. 3*a*). The carbonyl group (atoms C13 and O13) of the indoxyl moiety forms only intermolecular van der Waals interactions. *Via* the hydrogen bonds, each molecule is connected to two neighbouring molecules, leading to a helical arrangement propagating in the [010] direction. The resulting columns are connected to neighbouring columns by van der Waals (and electrostatic) interactions only. Within the helix, the angle between successive molecular planes is 85.05° (Fig. 4*b*). Graph-set analysis (Etter, 1990; Bernstein *et al.*, 1995) reveals two patterns, of *S*(6) and *C*(6) graph sets.

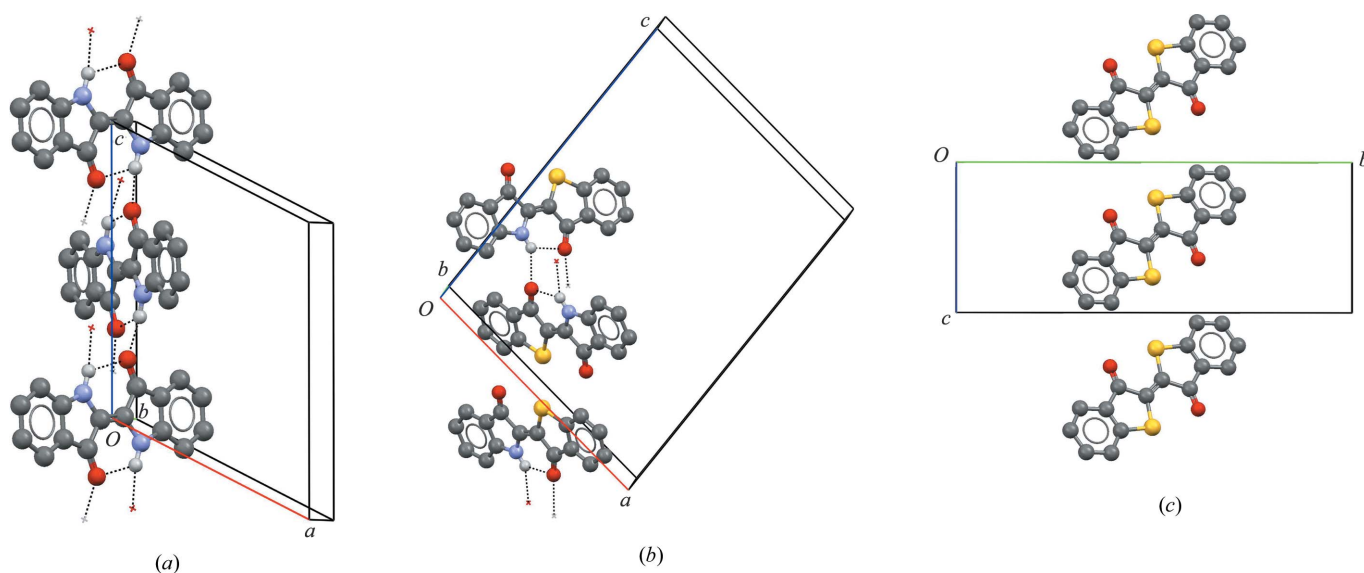


Figure 3
The molecular arrangements in (a) (II), (b) (I) and (c) (III). For (I), only the major occupancy components are shown.

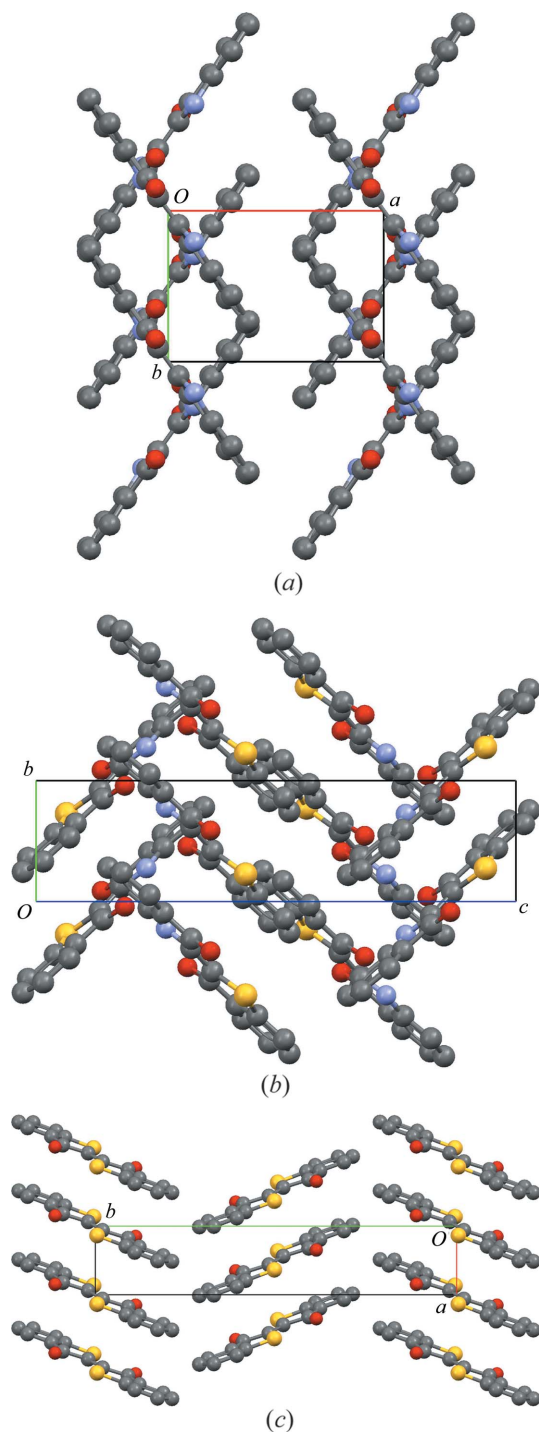


Figure 4
The crystal structures of (a) (II), (b) (I) and (c) (III). For (I), only the major occupancy components are shown.

The molecular packing of (I) is a combination of the arrangements found in the crystal structures of (II) (polymorph A; Süsse *et al.* 1988) and (III) (Haase-Wessel *et al.*, 1977). In indigo, (II), the molecules form hydrogen bonds on both sides of the molecule, with $S(6)$ and $C(6)$ graph sets as in (I). This results in a helical arrangement on both sides of the molecule, leading to a criss-cross pattern (Fig. 4a). In contrast,

thioindigo, (III), does not contain hydrogen bonds. The molecules form stacks, as in (I) and (II). Each molecule contacts two neighbouring molecules *via* $S \cdots S$ contacts, leading to chains with a herringbone arrangement (Fig. 3c and 4c). The space group of (I) is the same as for (II) and (III) ($P2_1/c$ or $P2_1/n$), but with $Z = 4$ (molecules on general positions) instead of $Z = 2$ (molecules on inversion centres).

Some years ago, Day & Motherwell (2006) showed by an experiment that crystal structure prediction by popular vote does not give good results. However, for monothioindigo a popular vote among crystallographers, based upon the structures of indigo and thioindigo, might probably have given the correct crystal packing.

Experimental

Small felted reddish violet crystals of (I) with sizes of about $1 \times 2 \times 10 \mu\text{m}$ were obtained from Professor Dr Wolfgang Lüttke, University of Göttingen.

Crystal data

$\text{C}_{16}\text{H}_9\text{NO}_2\text{S}$	$V = 1204.6 (4) \text{ \AA}^3$
$M_r = 279.30$	$Z = 4$
Monoclinic, $P2_1/n$	Synchrotron radiation
$a = 14.185 (3) \text{ \AA}$	$\lambda = 0.7084 \text{ \AA}$
$b = 4.6280 (9) \text{ \AA}$	$\mu = 0.27 \text{ mm}^{-1}$
$c = 18.483 (4) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 96.91 (3)^\circ$	$0.01 \times 0.002 \times 0.001 \text{ mm}$

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N11}-\text{H11} \cdots \text{O3}$	0.88	2.22	2.769 (4)	121
$\text{N11}-\text{H11} \cdots \text{O3}^\dagger$	0.88	2.24	2.992 (3)	143

Symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

Table 2

Comparison of the crystal structures of (I), (II) and (III).

	(II) [†]	(I) [‡]	(III) [§]
Compound name	Indigo	Monothioindigo	Thioindigo
Formula sum	$\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$	$\text{C}_{16}\text{H}_9\text{NO}_2\text{S}$	$\text{C}_{16}\text{H}_8\text{O}_2\text{S}_2$
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
Z	2	4	2
Z'	0.5	1	0.5
Site symmetry	$\bar{1}$	$\bar{1}$	$\bar{1}$
a (\AA)	9.24	14.185 (3)	3.981 (3)
b (\AA)	5.77	4.6280 (9)	20.65 (2)
c (\AA)	12.22	18.483 (4)	7.930 (7)
β ($^\circ$)	117.0	96.91 (3)	98.84 (5)
V (\AA^3)	580.497	1204.6 (4)	644.2 (10)
ρ (Mg m^{-3})	1.50	1.54	1.57
Distance between molecular mean planes (\AA)	3.345	3.411	3.526
Interplanar angle between neighbouring molecules ($^\circ$)	109.14	85.05	38.17
N—H distance (\AA)	0.98 (4)	0.88	
H \cdots O distance (\AA)	2.11 (4)	2.22	
N \cdots O distance (\AA)	2.862 (4)	2.769 (4)	
N—H \cdots O angle ($^\circ$)	132 (2)	121.0	

[†] CSD refcode INDIGO03 (Süsse *et al.*, 1988). [‡] This work. [§] CSD refcode SINDIG02 (Haase-Wessel *et al.*, 1977).

Data collection

Beamline X06SA (SLS, Villigen) 2453 independent reflections
 with Marresearch MAR225 CCD 1913 reflections with $I > 2\sigma(I)$
 area detector $R_{\text{int}} = 0.091$
 16267 measured reflections

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$ 57 restraints
 $wR(F^2) = 0.160$ H-atom parameters constrained
 $S = 1.03$ $\Delta\rho_{\text{max}} = 0.59 \text{ e } \text{Å}^{-3}$
 2453 reflections $\Delta\rho_{\text{min}} = -0.56 \text{ e } \text{Å}^{-3}$
 242 parameters

All H atoms were placed geometrically and refined using a riding model, with C—H = 0.95 Å and N—H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The molecules show orientational disorder, with a site-occupation factor of 0.962 (2) for the major occupied site. Bond lengths and 1,3 distances in both disorder components were restrained to be equal, with an effective standard uncertainty of 0.02 Å. The anisotropic displacement parameters of equivalent atoms in the two components were constrained to be equal.

Data collection: *XDS* (Kabsch, 1993); cell refinement: *XDS*; data reduction: *XDS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Version 2.2; Macrae *et al.*, 2008); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3356). Services for accessing these data are described at the back of the journal.

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