

1-[(2-Nitrophenyl)hydrazono]-1*H*-naphthalen-2-one
(Pigment Orange 2) from powder dataAlexandr V. Yatsenko,^{a*}
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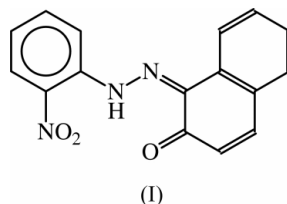
Key indicators

Powder X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.045
wR factor = 0.060For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound, $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3$, has been determined from X-ray powder data. The molecule is slightly non-planar. The structure adopts a stacking arrangement, with the stacks extended along [001]. The *AM1* calculations of the crystal electrostatic potential show that the crystal environment causes only a moderate (23%) increase in the molecular dipole moment of the title compound.

Comment

Azo derivatives of β -naphthols form a family of widely used dyes and pigments, and the title compound, (I), is a representative of this family.



All derivatives of 1-phenylazo-2-naphthol containing strong electron-acceptor substituents at the phenyl group are known to exist as hydrazone tautomers in solution (Koller & Zollinger, 1970; Korewa & Urbańska, 1972); this finding is in line with the results of crystallographic studies (Guggenberger & Teufer, 1975; Whitaker, 1978). Calculations using density functional theory (DFT) for an isolated molecule of (I) show that the hydrazone form is 40 kJ mol^{-1} more stable than the azo form. These calculations also predict a slightly non-planar geometry for this molecule owing to repulsion between the O1 and O2 atoms. In accordance with these predictions, the phenyl group in (I), as determined by the present study (Fig. 1), forms a dihedral angle of $13.7(2)^\circ$ with the naphthalene residue. Neighbouring molecules within the stack are related by the 2_1 screw axis, and the shortest intermolecular distances within the stack are $3.45(1) \text{ \AA}$. Two short intermolecular contacts [$\text{C5}-\text{H5}\cdots\text{O1}$ 2.59 and $\text{C14}-\text{H14}\cdots\text{O2}$ 2.61 \AA] are present in this structure. The *AM1*-calculated molecular dipole moment of (I) increases under the effect of the crystal environment (Yatsenko & Paseshnichenko, 2000) from 6.75 D for an isolated molecule to 8.27 D for a molecule within the crystal.

Experimental

The title compound, (I), was prepared according to the established procedure of Elbs *et al.* (1924).

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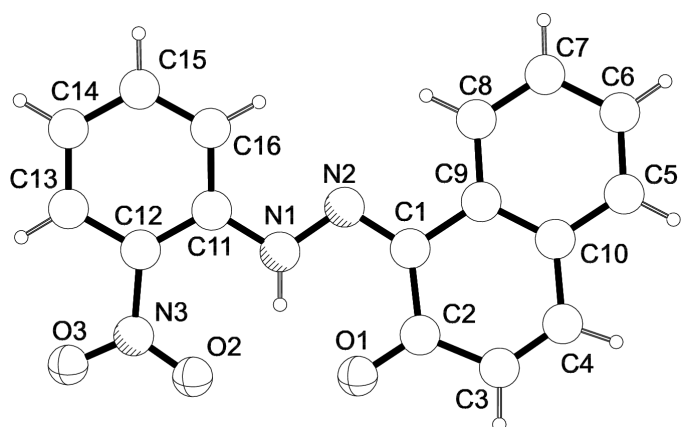


Figure 1
A view of (I) with the atom-numbering scheme.

Crystal data

$C_{16}H_{11}N_3O_3$
 $M_r = 293.28$
 Orthorhombic, $P2_12_12_1$
 $a = 15.036$ (5) Å
 $b = 12.722$ (4) Å
 $c = 7.042$ (3) Å
 $V = 1347.1$ (8) Å³
 $Z = 4$
 $D_x = 1.446$ Mg m⁻³
 Cu $K\alpha$ radiation

Cell parameters from 46 reflections
 $\theta = 4.1\text{--}25.9^\circ$
 $\mu = 0.85$ mm⁻¹
 $T = 295$ (2) K
 Orange-red
 Specimen shape: flat sheet
 $25 \times 25 \times 2.0$ mm
 Particle morphology: fibre-like needle

Data collection

DRON-3M diffractometer
 (Burevestnik, Russia)
 Specimen mounting: pressed as a thin layer in the specimen holder
 Specimen mounted in reflection mode

Absorption correction: none
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 8$
 $l = 0 \rightarrow 4$
 $2\theta_{\min} = 8.0$, $2\theta_{\max} = 70.0^\circ$
 Increment in $2\theta = 0.02^\circ$

Refinement

$R_p = 0.045$
 $R_{wp} = 0.060$
 $R_{exp} = 0.016$
 $S = 3.86$
 $2\theta_{\min} = 8.0$, $2\theta_{\max} = 66.0^\circ$
 Wavelength of incident radiation: 1.5418 Å
 Excluded region(s): 66.02–70.0
 Profile function: split-type pseudo-Voigt

112 parameters
 H-atom parameters not refined
 Weighting scheme based on measured s.u.'s
 $(\Delta/\sigma)_{\max} = 0.042$
 $\Delta\rho_{\max} = 0.55$ e Å⁻³
 $\Delta\rho_{\min} = -0.50$ e Å⁻³
 Preferred orientation correction: March-Dollase (Dollase, 1986) along [001], $G_1 = 1.210$ (1)

The orthorhombic cell dimensions of (I) were determined with *TREOR90* (Werner *et al.*, 1985) and refined to $M_{20} = 18$ and $F_{30} = 27(0.017,61)$ using the first 46 peak positions. The initial molecular model was built with *MOPAC7* (Stewart, 1993) on the AM1 level (Dewar *et al.*, 1985). The position and orientation of the molecule was determined using the grid-search procedure (Chernyshev & Schenk, 1998). The X-ray diffraction profile and the difference between the measured and calculated profiles after the Rietveld refinement are shown in Fig. 2; final $R_B = 0.076$. All atoms were refined isotropically and were gathered together into groups with a common U_{iso} parameter for each group. H atoms were placed in geometrically calculated positions and their isotropic displacement parameters were fixed. The planarity of the phenyl and nitro groups and of the

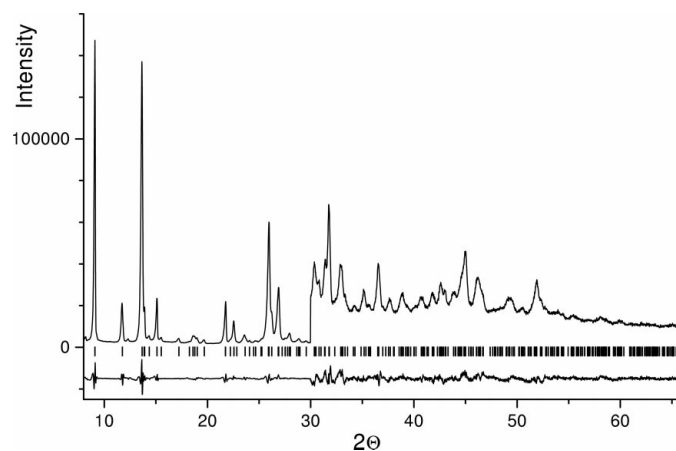


Figure 2
The Rietveld plot for (I) showing the observed and difference profiles. The reflection positions are shown above the difference profile.

naphthalene fragment was restrained. The anisotropy of diffraction-line broadening was approximated by a quartic form in hkl (Popa, 1998). The standard uncertainties obtained from the Rietveld refinement were corrected for the serial correlation effects (Bérar & Lelann, 1991). The DFT calculations were performed using a program provided by Dr D. N. Laikov (Laikov, 1997). The details of calculations employing the crystal electrostatic potential have been reported elsewhere (Yatsenko & Paseshnichenko, 2000).

Data collection: local program; cell refinement: *LSPAID* (Visser, 1986); program(s) used to solve structure: *MRIA* (Zlokazov & Chernyshev, 1992); program(s) used to refine structure: *MRIA*; molecular graphics: *PLUTON* (Spek, 1992); software used to prepare material for publication: *PARST* (Nardelli, 1983).

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