π–π Stacks and C–H···O bonded sheets in 4-[(2-nitrophenyl)hydrazono]-4H-naphthalen-1-one

A. V. Yatsenko* and K. A. Paseshnichenko

Chemistry Department, Moscow State University, 119899 Moscow, Russia

Correspondence e-mail: yatsenko@biocryst.phys.msu.su

Key indicators

Single-crystal X-ray study
$T = 293$ K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.108
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{16}H_{11}N_3O_3$, (I), exists in crystals as the pure hydrazone tautomer. Molecules form stacks stretched along [100]. $AM1$ calculations of the crystal electrostatic potential show that the crystal environment causes only a 24% increase in the molecular dipole moment of (I).
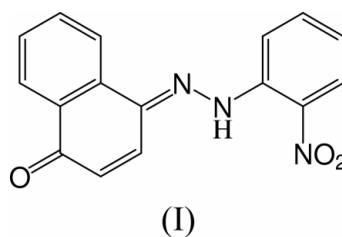
Comment

Azo derivatives of α- and β-naphthols form a family of widely used dyes and pigments, but structure determinations of the derivatives of α-naphthol have not been reported up to now.

(I)

The title compound, (I), is known to exist in solution as the hydrazone tautomer (Koller & Zollinger, 1970; Korewa & Urbańska, 1972). The density functional theory (DFT) calculations for the isolated molecule showed that the hydrazone form is 28 kJ mol^{-1} more stable than the azo form.

The molecule of (I) is close to being planar; its structure is shown in Fig. 1 and selected geometrical parameters are given in Table 1. The bond dimensions in the keto–hydrazone O1—C1—C2—C3—C4—N2—N1 chain indicate alternation of single and double bonds, thus only a moderate charge transfer from the hydrazone moiety to the keto group takes place. Neighbouring molecules within the stack are related by inversion centres, with interplanar distances of 3.347 (1) and 3.411 (1) Å. The nitro group forms an intramolecular hydrogen bond with the hydrazone H atom, thus precluding the formation of intermolecular hydrogen bonds. As shown in Fig. 2, the molecules are gathered together by C—H···O contacts to form flat sheets.

$AM1$ (Dewar et al., 1985) calculations predict that under the effect of the crystal electrostatic potential (Yatsenko & Paseshnichenko, 2000) the molecular dipole moment of (I) increases from 5.64 D for an isolated molecule to 6.99 D for a molecule within the crystal.

Experimental

Compound (I) was prepared according to the established procedure of Elbs et al. (1924). Single crystals were grown by slow evaporation of a chloroform solution of (I). The DFT calculations were performed using the program provided by Dr D. N. Laikov (1997). Details of

calculations employing the crystal electrostatic potentials have been reported elsewhere (Yatsenko & Paseshnichenko, 2000).

Crystal data

$C_{16}H_{11}N_3O_3$
$M_r = 293.28$
Monoclinic, $P2_1/n$
$a = 7.328 (2)$ Å
$b = 16.366 (4)$ Å
$c = 11.131 (3)$ Å
$\beta = 99.33 (2)°$
$V = 1317.3 (6)$ Å^3
$Z = 4$

$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22
    reflections
$\theta = 14.7$–$16.3°$
$\mu = 0.11$ mm^{-1}
$T = 293 (2)$ K
Needle, dark red
$0.55 \times 0.16 \times 0.09$ mm

Data collection

Enraf–Nonius CAD-4
    diffractometer
ω scans
3173 measured reflections
3025 independent reflections
2041 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

$\theta_{max} = 27.5°$
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 14$
3 standard reflections
    frequency: 120 min
    intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 1.31$
3025 reflections
244 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.04P)^2]$
    where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.20$ e Å^{-3}
$\Delta\rho_{min} = -0.16$ e Å^{-3}
Extinction correction: $SHELXL97$
Extinction coefficient: 0.0027 (8)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.2235 (17)	C1—C9	1.483 (2)
N1—N2	1.3462 (17)	C2—C3	1.339 (2)
N2—C4	1.3053 (17)	C3—C4	1.451 (2)
C1—C2	1.446 (2)	C4—C10	1.4703 (19)
N2—N1—C11	118.67 (12)	N2—C4—C3	126.51 (13)
C4—N2—N1	118.69 (12)	N2—C4—C10	115.68 (12)

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O2	1.05 (2)	1.76 (2)	2.594 (2)	133 (1)
C2—H2$\cdots$O3^i	0.88 (2)	2.58 (2)	3.233 (2)	131 (1)
C6—H6$\cdots$O1^{ii}	0.93 (2)	2.51 (2)	3.426 (2)	169 (1)
C13—H13$\cdots$O2^{iii}	0.96 (2)	2.65 (2)	3.323 (2)	128 (1)
C15—H15$\cdots$O1^{iv}	0.92 (2)	2.66 (2)	3.474 (2)	148 (1)

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *PROFIT* (Streltsov & Zavodnik, 1989); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2001).
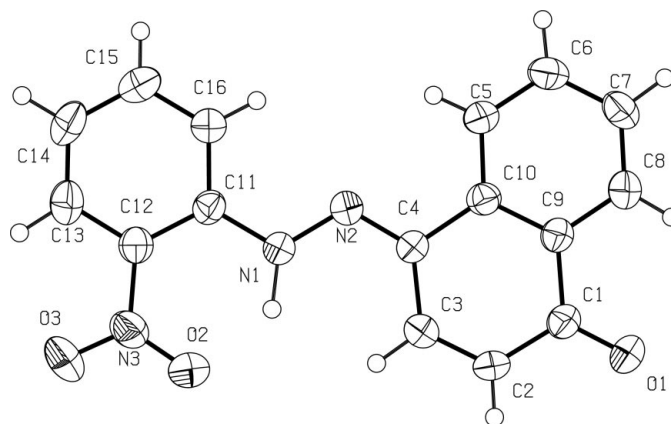

Figure 1
A view of (I) with 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.
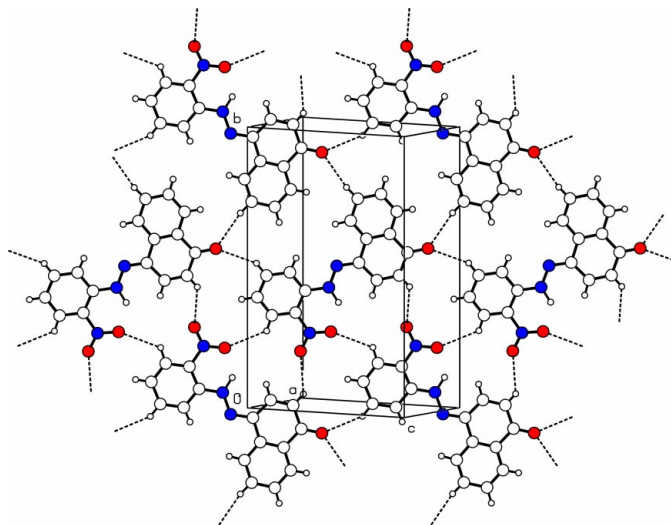

Figure 2
C—H$\cdots$O bonded sheets in the structure of (I).

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