

Anthracene-9-carbaldehyde hydrazone

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Key indicators

Single-crystal X-ray study

T = 291 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.052

wR factor = 0.140

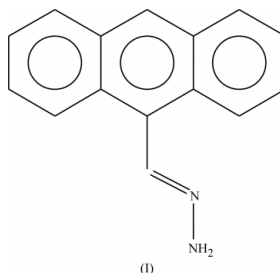
Data-to-parameter ratio = 12.3

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

In the title compound, $\text{C}_{15}\text{H}_{12}\text{N}_2$, the geometric parameters are normal, within experimental error. The molecules are arranged in pairs, with their hydrazone groups oriented towards one another.

Comment

During our investigation of the chemical and electrochemical properties of the azine grouping $>\text{C}=\text{N}-\text{N}=\text{C}<$ (Riedl *et al.*, 1996; Zuman & Ludvík, 2000), various azine and hydrazone derivatives have been synthesized, including the title compound, (I), derived from anthracene-9-carbaldehyde.



For comparison with the distances in (I), a search of the Cambridge Structural Database (CSD, Version 5.24; Allen, 2002) was carried out and yielded 24 hits. The search considered structures containing anthracene, not involved in π -bonding with a metal, and with *R* factors < 0.09. The bond lengths within the anthracene rings of (I) are in accordance with those found in the search, except for slight deviations of the bond-lengths of the pairs C9–C11, C9–C13 and C10–C12, C10–C14 (Fig. 1), which are $\sim 0.022 \text{ \AA}$ longer and 0.008 \AA shorter, respectively, than in pure anthracene. The reason why the chemically equivalent bonds C9–C11, C9–C13 are longer than C10–C12, C10–C14 (Table 1) is probably due to the substituent on C9.

Neither atom N1 nor atom N2 lies in the plane of the central aromatic ring *A* (C9/C11/C12/C10/C14/C13). The dihedral angle between the plane through atoms N1, C15, C9 and plane *A* is $42.9(2)^\circ$. The N1–N2 bond length of $1.387(2) \text{ \AA}$ is significantly longer than the N=N bond length in azo compounds ($\sim 1.25 \text{ \AA}$), as shown by a search of the CSD. [Compounds with a fragment $\text{C}\cdots\text{C}\cdots\text{N}\cdots\text{N}\cdots\text{C}\cdots\text{C}$ were searched for, with coordination number 3 for C and 2 for N. The value of $\sim 1.25 \text{ \AA}$ corresponds to the maximum (more than 700 hits) in the distribution of N \cdots N bond lengths.] On the other hand the N1–N2 bond length is shorter than that in the compounds containing hydrazinium(1+) molecules where the average value is $1.435(7) \text{ \AA}$, according to 36 hits from the CSD.

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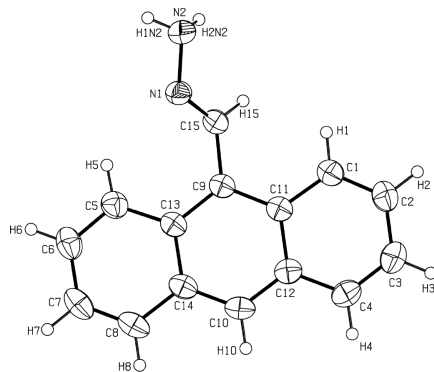


Figure 1
View of the title molecule, with 40% probability displacement ellipsoids (*PLATON*; Spek, 2002).

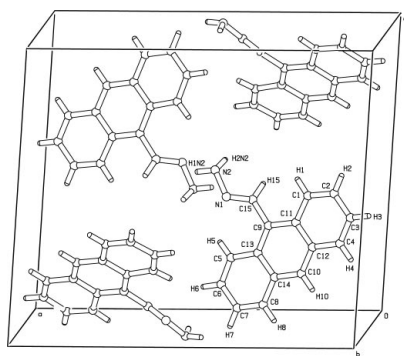


Figure 2
Crystal packing in the unit cell (*PLATON*; Spek, 2002).

This comparison shows that the N–N bond in (I) (Table 1) has a bond order close to one. The bond length between atoms C15 and N1 [1.272 (2) Å] corresponds, however, to a typical double bond, that is ~ 1.28 Å (Box & Yu, 1997).

The hydrazone groups are oriented towards each other, ordering the molecules into hydrogen bonded pairs (Fig. 2). The geometry of the N2–H1N2 \cdots N1 contact points to a weak hydrogen bond (Table 2).

Experimental

9-Anthraldehyde (1.4 g) was diluted in 30 ml of ethanol, and 0.34 ml of hydrazine hydrate was added under heating. After slow cooling the mixture was kept in a refrigerator overnight. The crystals formed were isolated, washed by ethanol and dried. The yield was 1 g of the title compound, whose identity and purity was checked by thin-layer chromatography and NMR spectra. If one-half of the quantity of hydrazine hydrate was used and the mixture was refluxed for 5 h, the corresponding azine was produced. However, no suitable crystals could be obtained.

Crystal data

C₁₅H₁₂N₂
M_r = 220.27
 Monoclinic, *P*₂₁/*c*
a = 17.7211 (9) Å
b = 3.9082 (2) Å
c = 16.4115 (9) Å
 β = 103.856 (3)°
V = 1103.55 (10) Å³
Z = 4
D_x = 1.325 Mg m⁻³

Cell parameters determined with
 Mo K α radiation
 Mo K α radiation
 Cell parameters from 4704
 reflections
 θ = 1.0–26.0°
 μ = 0.08 mm⁻¹
T = 291 (1) K
 Plate, yellow
 0.30 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
 ω scans
 Absorption correction: none
 2169 measured reflections
 2169 independent reflections

1628 reflections with $I > 2\sigma(I)$
 $\theta_{\max} = 26.0^\circ$
 $h = 0 \rightarrow 21$
 $k = -4 \rightarrow 4$
 $l = -20 \rightarrow 19$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.140$
 $S = 1.10$
 2169 reflections
 177 parameters
 H atoms treated by a mixture of
 independent and constrained
 refinement

$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2 + 0.0918P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.107 (10)

Table 1

Selected geometric parameters (Å, °).

C1–C2	1.357 (2)	C9–C11	1.415 (2)
C1–C11	1.429 (2)	C9–C13	1.419 (2)
C2–C3	1.409 (2)	C9–C15	1.471 (2)
C3–C4	1.350 (2)	C10–C14	1.387 (2)
C4–C12	1.425 (2)	C10–C12	1.388 (2)
C5–C6	1.360 (2)	C11–C12	1.438 (2)
C5–C13	1.427 (2)	C13–C14	1.436 (2)
C6–C7	1.405 (3)	C15–N1	1.2709 (19)
C7–C8	1.346 (3)	N1–N2	1.3870 (19)
C8–C14	1.432 (2)		
N1–C15–C9	123.94 (15)	C15–N1–N2	116.84 (15)
N1–C15–H15	119.2 (10)	N1–N2–H1N2	108.9 (15)
C9–C15–H15	116.8 (10)	N1–N2–H2N2	112.5 (15)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H \cdots <i>A</i>	<i>D</i> –H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> –H \cdots <i>A</i>
N2–H1N2 \cdots N1 ⁱ	0.86 (2)	2.47 (2)	3.233 (2)	147.9 (19)

Symmetry code: (i) $1 - x, 2 - y, 1 - z$.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002); software used to prepare material for publication: *SHELXL97*.

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