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Tautomerism in 10-(hydroxyimino)-phenanthren-9-one

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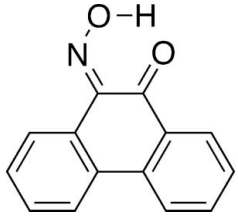
Key indicators: single-crystal X-ray study; T = 90 K; mean σ(C–C) = 0.004 Å; disorder in main residue; R factor = 0.036; wR factor = 0.099; data-to-parameter ratio = 6.4.

In the title compound, $C_{14}H_9NO_2$, a static disorder exists between the keto–oxime and hydroxy–nitroso tautomers, in an approximate ratio of 4.6:1, based on refined occupancies for disordered parts. No intermolecular hydrogen bonding is present in the crystal structure. Instead, both tautomers exhibit similar intramolecular O—H···O hydrogen bonds.

Related literature

For information on tautomerization in *ortho*-hydroxynitroso aromatic compounds, see: Enchev *et al.* (2003); Terent'ev & Stankyavichyus (1988). For the role of *ortho*-hydroxynitroso aromatic compounds in metal complexation and in photochromic spirooxazines, see: Barjesteh *et al.* (1996); Patel *et al.* (2005, 2010). For the spectrochemical characterization of the title compound, see: Kumar *et al.* (2009).



Experimental

Crystal data

$C_{14}H_9NO_2$
M_r = 223.22
Orthorhombic, $Pca2_1$
a = 17.4505 (15) Å
b = 3.7875 (3) Å
c = 15.1669 (13) Å
V = 1002.44 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 90 K
0.24 × 0.10 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.976, T_{max} = 0.994
16616 measured reflections
1068 independent reflections
989 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.07
1068 reflections
166 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.84	1.76	2.499 (8)	146
O1A—H1A···O2A	0.84	1.93	2.54 (2)	128

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Partial support of this work was provided by the University at Buffalo, The State University of New York.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2448).

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supplementary materials

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Comment

The title compound (Fig. 1) is an *ortho*-hydroxynitroso aromatic compound, which may have a role in metal complexation and in photochromic spirooxazines (Barjesteh *et al.*, 1996; Patel *et al.*, 2005, 2010). A tautomeric disorder was observed in this structure (Enchev *et al.*, 2003; Terent'ev & Stankyavichyus, 1988). Without accounting for the disorder, a Q-peak of approximately 0.9 electron/Å^3 was located at the position of O2A in the disorder model. Prior to modeling the disorder, R_1 residual was approximately 0.06. With the chemically sensible disorder model, the final residual is R_1 = 0.0361, justifying the reduced number of parameters and minimal *EADP* constraints and *FLAT* restraint (see *Experimental*). The final refinement indicated the two tautomers are present in an 0.827 (3) to 0.173 (3) ratio.

Experimental

The title compound was synthesized according to a previously published procedure (Terent'ev & Stankyavichyus, 1988). Briefly, commercially available phenanthrene-9,10-quinone (1.500 g, 7.20 mmol) was refluxed in ethanol (100 ml) and chloroform (20 ml). To this solution was added hydroxylamine hydrochloride (0.500 g, 7.20 mmol dissolved in 20 ml of water) dropwise. After refluxing overnight, solvent was removed and the resulting orange solid was recrystallized from aqueous ethanol (1.086 g, 68%). Spectral characterization matched that in the literature (Kumar *et al.*, 2009).

Refinement

All H atoms were initially located in a difference Fourier map and were refined with a riding model. H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances fixed to 0.95 Å and O—H distances fixed to 0.84 Å. U_{iso} values were fixed as U_{iso}(H) = 1.2U_{eq}(parent C) and U_{iso}(H) = 1.5U_{eq}(parent O). Atoms N1A, O2A, H1A and O1A were restrained to be coplanar, and the same anisotropic displacement parameters were used for pairs of disordered atoms N1/O1A, O2/O2A and N1A/O1. Measured Friedel pairs (983) were merged in the final refinement.

Computing details

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

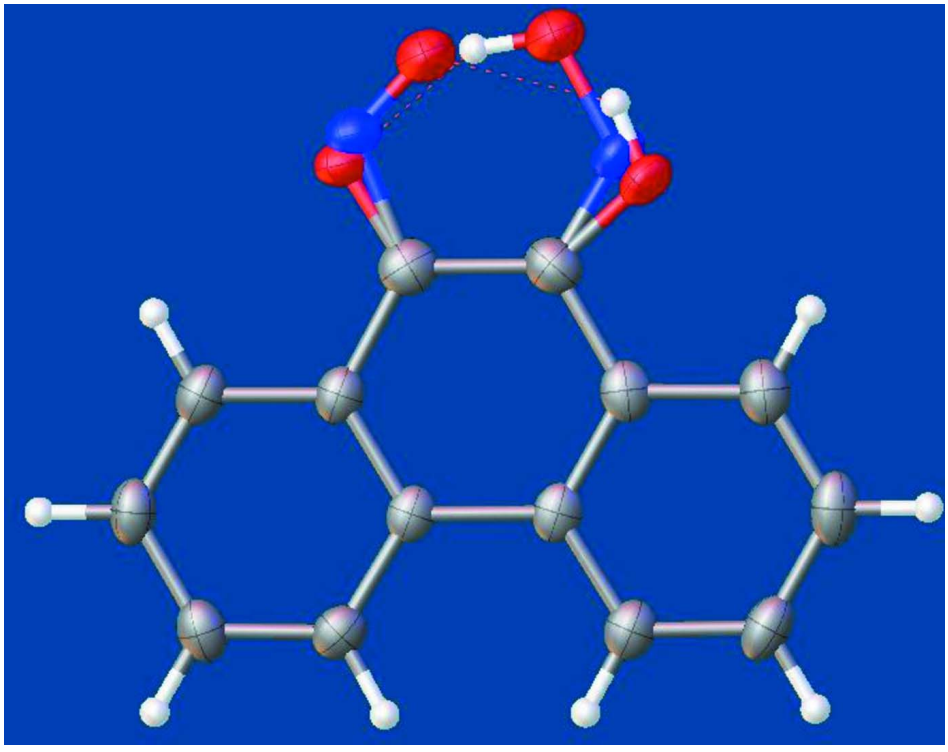

Figure 1

ORTEP view (Dolomanov *et al.*, 2009) of the title molecule. Dashed lines represent intramolecular hydrogen bonds.

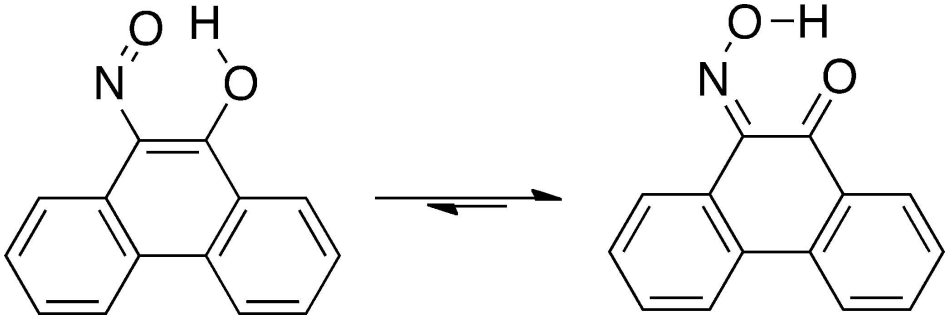

Figure 2

The tautomerism in the title compound.

10-(Hydroxyimino)phenanthren-9-one

Crystal data

$C_{14}H_9NO_2$
$M_r = 223.22$
Orthorhombic, $Pca2_1$
Hall symbol: P 2c -2ac
$a = 17.4505$ (15) Å
$b = 3.7875$ (3) Å
$c = 15.1669$ (13) Å
$V = 1002.44$ (15) Å^3
$Z = 4$
$F(000) = 464$
$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 250 reflections
$\theta = 2.3$–$26.0°$
$\mu = 0.10$ mm^{-1}
$T = 90$ K
Plate, yellow
0.24 × 0.10 × 0.06 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: rotating anode
Optics monochromator
w scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
T_{min} = 0.976, T_{max} = 0.994
16616 measured reflections
1068 independent reflections
989 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 26.4°, θ_{min} = 2.3°
h = −21→21
k = −4→4
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.099
S = 1.07
1068 reflections
166 parameters
2 restraints
18 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.3852P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Special details

Experimental. Data were collected with five ω scans in 0.5° increments with 20 s. exposures per degree. Crystal-to-detector distance was 40 mm. 18620 full and partial reflections were integrated.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.7027 (5)	0.491 (3)	0.5919 (3)	0.0366 (12)	0.827 (5)
O1A	0.5549 (10)	0.199 (7)	0.6677 (16)	0.0362 (9)	0.173 (5)
H1A	0.5911	0.2311	0.7033	0.054*	0.173 (5)
O2	0.63991 (15)	0.2459 (9)	0.72678 (18)	0.0500 (8)	0.827 (5)
H2	0.6762	0.3150	0.6947	0.075*	0.827 (5)
O2A	0.6923 (8)	0.414 (5)	0.6788 (9)	0.0500 (8)	0.173 (5)
N1	0.5786 (2)	0.1557 (14)	0.6749 (3)	0.0362 (9)	0.827 (5)
N1A	0.707 (4)	0.494 (19)	0.611 (3)	0.0366 (12)	0.173 (5)
C1	0.64614 (15)	0.4012 (7)	0.5486 (2)	0.0309 (6)	
C2	0.64506 (14)	0.4585 (7)	0.45317 (18)	0.0258 (6)	
C3	0.70969 (14)	0.6130 (7)	0.4138 (2)	0.0286 (6)	
H3	0.7523	0.6791	0.4492	0.034*	
C4	0.71138 (15)	0.6687 (7)	0.3247 (2)	0.0320 (6)	
H4	0.7554	0.7696	0.2979	0.038*	
C5	0.64841 (16)	0.5767 (7)	0.27380 (19)	0.0312 (6)	
H5	0.6495	0.6167	0.2120	0.037*	
C6	0.58366 (15)	0.4269 (7)	0.31197 (19)	0.0281 (6)	
H6	0.5407	0.3701	0.2762	0.034*	
C7	0.58119 (14)	0.3592 (7)	0.40243 (18)	0.0244 (6)	
C8	0.51377 (13)	0.1929 (7)	0.44476 (18)	0.0257 (6)	
C9	0.45080 (15)	0.0821 (7)	0.3952 (2)	0.0292 (6)	
H9	0.4511	0.1139	0.3330	0.035*	

C10	0.38781 (15)	−0.0737 (8)	0.4350 (2)	0.0325 (7)
H10	0.3458	−0.1498	0.4000	0.039*
C11	0.38582 (16)	−0.1190 (8)	0.5257 (2)	0.0356 (7)
H11	0.3421	−0.2200	0.5531	0.043*
C12	0.44774 (15)	−0.0164 (8)	0.5756 (2)	0.0328 (7)
H12	0.4466	−0.0500	0.6377	0.039*
C13	0.51259 (15)	0.1372 (7)	0.53659 (19)	0.0286 (6)
C14	0.57893 (17)	0.2359 (7)	0.59059 (19)	0.0319 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0292 (16)	0.0496 (13)	0.031 (3)	−0.0041 (12)	−0.007 (2)	−0.003 (3)
O1A	0.023 (2)	0.050 (2)	0.0349 (16)	−0.001 (2)	−0.0061 (19)	0.0011 (15)
O2	0.0401 (14)	0.073 (2)	0.0368 (15)	−0.0153 (15)	−0.0084 (11)	0.0053 (14)
O2A	0.0401 (14)	0.073 (2)	0.0368 (15)	−0.0153 (15)	−0.0084 (11)	0.0053 (14)
N1	0.023 (2)	0.050 (2)	0.0349 (16)	−0.001 (2)	−0.0061 (19)	0.0011 (15)
N1A	0.0292 (16)	0.0496 (13)	0.031 (3)	−0.0041 (12)	−0.007 (2)	−0.003 (3)
C1	0.0330 (15)	0.0237 (13)	0.0359 (15)	0.0060 (11)	0.0007 (12)	−0.0048 (12)
C2	0.0236 (12)	0.0177 (12)	0.0360 (15)	0.0036 (10)	0.0021 (10)	−0.0013 (12)
C3	0.0228 (13)	0.0207 (13)	0.0424 (17)	0.0024 (9)	0.0010 (11)	−0.0014 (12)
C4	0.0256 (13)	0.0234 (13)	0.0470 (17)	0.0010 (10)	0.0088 (13)	0.0020 (12)
C5	0.0320 (13)	0.0253 (14)	0.0364 (16)	0.0055 (11)	0.0077 (12)	0.0058 (12)
C6	0.0253 (13)	0.0230 (13)	0.0360 (15)	0.0049 (10)	−0.0024 (11)	−0.0015 (12)
C7	0.0215 (13)	0.0152 (12)	0.0364 (15)	0.0056 (9)	0.0022 (10)	−0.0026 (11)
C8	0.0222 (12)	0.0152 (12)	0.0397 (16)	0.0066 (10)	0.0035 (11)	−0.0020 (11)
C9	0.0253 (12)	0.0214 (13)	0.0408 (16)	0.0050 (10)	0.0015 (12)	−0.0016 (12)
C10	0.0214 (12)	0.0233 (13)	0.0530 (19)	0.0023 (10)	0.0000 (12)	−0.0045 (12)
C11	0.0272 (14)	0.0235 (14)	0.056 (2)	0.0049 (11)	0.0128 (12)	0.0020 (13)
C12	0.0334 (14)	0.0235 (13)	0.0415 (17)	0.0033 (11)	0.0090 (12)	0.0004 (12)
C13	0.0296 (14)	0.0192 (12)	0.0370 (15)	0.0071 (10)	0.0074 (11)	−0.0014 (12)
C14	0.0384 (15)	0.0259 (14)	0.0315 (15)	0.0033 (12)	0.0033 (11)	−0.0010 (12)

Geometric parameters (Å, º)

O1—C1	1.233 (8)	C5—C6	1.391 (4)
O1A—C14	1.25 (2)	C5—H5	0.9500
O1A—H1A	0.8400	C6—C7	1.396 (4)
O2—N1	1.371 (5)	C6—H6	0.9500
O2—H2	0.8400	C7—C8	1.481 (3)
O2A—N1A	1.11 (5)	C8—C9	1.396 (4)
N1—C14	1.314 (6)	C8—C13	1.409 (4)
N1A—C1	1.46 (5)	C9—C10	1.386 (4)
C1—C2	1.464 (4)	C9—H9	0.9500
C1—C14	1.474 (4)	C10—C11	1.386 (4)
C2—C3	1.404 (4)	C10—H10	0.9500
C2—C7	1.406 (4)	C11—C12	1.376 (4)
C3—C4	1.369 (4)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.403 (4)
C4—C5	1.387 (4)	C12—H12	0.9500

C4—H4	0.9500	C13—C14	1.467 (4)
C14—O1A—H1A	109.5	C2—C7—C8	120.4 (2)
C14—N1—O2	119.9 (4)	C9—C8—C13	118.4 (3)
O2A—N1A—C1	112 (5)	C9—C8—C7	121.3 (2)
O1—C1—C2	119.7 (4)	C13—C8—C7	120.3 (2)
N1A—C1—C2	128 (2)	C10—C9—C8	121.1 (3)
O1—C1—C14	121.6 (4)	C10—C9—H9	119.4
N1A—C1—C14	114 (2)	C8—C9—H9	119.4
C2—C1—C14	118.7 (2)	C11—C10—C9	120.3 (3)
C3—C2—C7	121.1 (2)	C11—C10—H10	119.8
C3—C2—C1	118.1 (2)	C9—C10—H10	119.8
C7—C2—C1	120.8 (2)	C12—C11—C10	119.4 (3)
C4—C3—C2	120.1 (3)	C12—C11—H11	120.3
C4—C3—H3	120.0	C10—C11—H11	120.3
C2—C3—H3	120.0	C11—C12—C13	121.2 (3)
C3—C4—C5	119.6 (3)	C11—C12—H12	119.4
C3—C4—H4	120.2	C13—C12—H12	119.4
C5—C4—H4	120.2	C12—C13—C8	119.4 (3)
C4—C5—C6	121.0 (3)	C12—C13—C14	120.4 (3)
C4—C5—H5	119.5	C8—C13—C14	120.2 (2)
C6—C5—H5	119.5	O1A—C14—C13	103.3 (9)
C5—C6—C7	120.6 (3)	N1—C14—C13	118.8 (3)
C5—C6—H6	119.7	O1A—C14—C1	135.9 (10)
C7—C6—H6	119.7	N1—C14—C1	121.4 (3)
C6—C7—C2	117.7 (2)	C13—C14—C1	119.7 (2)
C6—C7—C8	121.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.84	1.76	2.499 (8)	146
O1*A*—H1*A*···O2*A*	0.84	1.93	2.54 (2)	128