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4,5-Dihydroxy-1-nitroanthracene-9,10-dione

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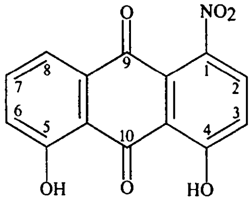
Abstract

In the search for new tautomeric systems among anthraquinone derivatives, we carried out an X-ray structural study of the title compound, 4,5-dihydroxy-1-nitro-9,10-anthraquinone, $C_{14}H_7NO_6$. The asymmetric unit contains two symmetry-independent molecules. Both anthraquinone tricyclic units (ATU) adopt a nearly planar conformation. The influence of the nitro group does not cause any fundamental changes in the distribution of the bond lengths in the intramolecular system of hydrogen bonds.

Comment

The bond dimensions in molecules 1 and 2 of the title compound, (I), are essentially the same; the r.m.s. difference of equivalent bond lengths is 0.006 Å. The main difference between the molecules seems to be due to some rotational disorder of the nitro group in molecule 1 [the 'effective' dihedral angle between the nitro group and the ATU is 85 (1)°], which leads to the splitting of the O9 and C9 atoms over two sets of sites above and below the molecular plane. This disorder manifests itself as a stretching of the displacement ellipsoids of O9, C9, O11 and O12. As a result, the ATU of molecule 1 becomes essentially planar [atom C5 has the maximum deviation from the least-squares plane of 0.038 (3) Å] and the bonds involving the C9 atom are 0.013–0.010 Å shorter than those in molecule 2. In molecule 2, the dihedral angle between the nitro group and the ATU is fixed at 73 (1)°, the displacement of atoms C9*A* and O9*A* from the tricyclic plane being 0.073 (3) and 0.244 (2) Å, respectively, thus minimizing the repulsion from the nitro group. The outer rings in molecules 1 and 2 are mutually inclined at angles of only 2.1 (5) and 0.7 (4)°, respectively, indicating the absence of any considerable steric hindrance between the *peri* substituents.



(I)

The bond lengths in both ATU's of this structure essentially do not differ from those observed in other structures containing the 1,8-dihydroxy-9,10-anthracenedione moiety reported in the literature; 1,8-dinitro-4,5-dihydroxyanthraquinone (Brown & Colclough, 1983), 7-methoxy-2-methyl-4,5-dihydroxyanthraquinone (Ulický, Kožíšek & Ječný, 1991) and 1-acetyl-2,4,5,7-tetrahydroxyanthraquinone (Ulický, Kettmann, Soldánová & Betina, 1987). Only the mean disparity of the carbonyl bonds, C9═O9 and C10═O10, in the structure reported herein is noticeably less than in the former two structures; 0.039 (2) Å compared with 0.048 and 0.053 Å, respectively.

The average O4···O10 distance for the two molecules is 0.023 Å shorter than the mean O5···O10 contact distance, indicating some strengthening of the former hydrogen bond. The PM3 computations (results deposited) carried out with the *MOPAC*6.0 package (Stewart, 1990) have given nearly the same value for the O···O distance disproportion (0.025 Å). The energies of tautomerization into *ana*-quinonoid forms have also been calculated and the 4,9-tautomer appears to be only 1.5 kJ mol^{-1} more stable than the 5,9-tautomer. Thus, the nitro group, playing a σ-acceptor role, does not cause any fundamental changes in the electron-density distribution in the system of resonance-assisted hydrogen bonds.

Molecules 1 and 2 are arranged in pairs into 'head-to-tail' dimers (Fig. 1). The shortest intermolecular C···C distance in the dimer is 3.454 (4) Å and the shortest interdimer C···C spacing is 3.309 (4) Å. There are no intermolecular hydrogen bonds.

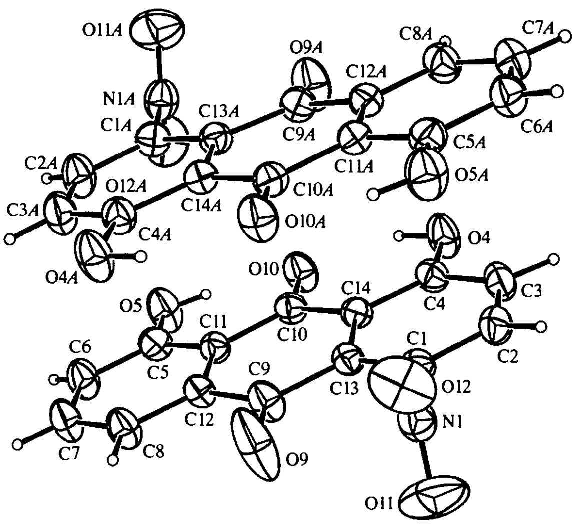


Fig. 1. The two independent molecules of 4,5-dihydroxy-1-nitroanthracene-9,10-dione showing 40% probability displacement ellipsoids and the dimeric arrangement.

Experimental

A sample of 4,5-dihydroxy-1-nitroanthracene-9,10-dione, (I), obtained from the collection of the Institute of Organic Intermediates and Dyes, was crystallized from toluene.

Crystal data

$C_{14}H_7NO_6$
$M_r = 285.21$
Monoclinic
$P2_1/n$
$a = 10.739\,(3)$ Å
$b = 15.452\,(5)$ Å
$c = 14.522\,(5)$ Å
$\beta = 109.59\,(3)°$
$V = 2270.3\,(12)$ Å^3
$Z = 8$
$D_x = 1.669$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.7–18.0°$
$\mu = 0.134$ mm^{-1}
$T = 295\,(2)$ K
Prism
0.55 × 0.30 × 0.25 mm
Yellow–orange

Data collection

Enraf–Nonius CAD-4 four-circle diffractometer
Profile data from ω scans
Absorption correction: none
8309 measured reflections
4004 independent reflections
2304 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0310$
$\theta_{\rm max} = 24.97°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 18$
$l = -17 \rightarrow 16$
3 standard reflections frequency: 90 min intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0440$
$wR(F^2) = 0.1204$
$S = 0.912$
4004 reflections
435 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.066P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.063$
$\Delta\rho_{\rm max} = 0.226$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.191$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Molecule 1				
N1	0.4532 (2)	0.0590 (1)	0.1089 (2)	0.0500 (5)
O11	0.3870 (3)	0.0262 (1)	0.0327 (2)	0.1010 (8)
O12	0.4827 (2)	0.0230 (1)	0.1865 (2)	0.0853 (7)
C1	0.5041 (2)	0.1472 (1)	0.1053 (2)	0.0363 (5)
C2	0.6301 (2)	0.1524 (2)	0.0996 (2)	0.0442 (6)
C3	0.6815 (2)	0.2314 (2)	0.0918 (2)	0.0461 (6)
O4	0.6693 (2)	0.3818 (1)	0.0830 (1)	0.0564 (5)
C4	0.6111 (2)	0.3069 (1)	0.0912 (2)	0.0390 (5)
O5	0.2320 (2)	0.5286 (1)	0.0840 (2)	0.0598 (6)
C5	0.1954 (2)	0.4483 (1)	0.0978 (2)	0.0414 (6)
C6	0.0708 (2)	0.4396 (2)	0.1069 (2)	0.0497 (7)
C7	0.0223 (2)	0.3600 (2)	0.1177 (2)	0.0528 (7)
C8	0.0954 (2)	0.2863 (2)	0.1198 (2)	0.0467 (6)
O9	0.2485 (2)	0.1433 (1)	0.1180 (2)	0.1009 (9)
C9	0.2953 (2)	0.2127 (1)	0.1126 (2)	0.0445 (6)
O10	0.4529 (2)	0.4532 (1)	0.0874 (1)	0.0496 (4)
C10	0.4056 (2)	0.3812 (1)	0.0951 (2)	0.0363 (5)
C11	0.2727 (2)	0.3744 (1)	0.1013 (2)	0.0344 (5)
C12	0.2199 (2)	0.2928 (1)	0.1120 (2)	0.0354 (5)
C13	0.4295 (2)	0.2197 (1)	0.1056 (2)	0.0338 (5)
C14	0.4829 (2)	0.3024 (1)	0.0984 (2)	0.0335 (5)
Molecule 2				
N1*A*	0.5027 (2)	0.5423 (1)	0.3461 (2)	0.0497 (5)
O11*A*	0.5834 (2)	0.5723 (1)	0.4190 (2)	0.0816 (7)
O12*A*	0.4510 (2)	0.5828 (1)	0.2711 (2)	0.0751 (6)
C1*A*	0.4545 (2)	0.4540 (1)	0.3503 (2)	0.0398 (6)
C2*A*	0.3296 (2)	0.4475 (2)	0.3566 (2)	0.0498 (7)
C3*A*	0.2793 (3)	0.3689 (2)	0.3660 (2)	0.0506 (7)
O4*A*	0.2946 (2)	0.2198 (1)	0.3807 (1)	0.0580 (5)
C4*A*	0.3514 (2)	0.2938 (1)	0.3696 (2)	0.0408 (6)
O5*A*	0.7236 (2)	0.0728 (1)	0.3683 (1)	0.0559 (5)
C5*A*	0.7641 (2)	0.1529 (1)	0.3578 (2)	0.0404 (6)
C6*A*	0.8895 (2)	0.1609 (2)	0.3503 (2)	0.0473 (6)
C7*A*	0.9386 (2)	0.2403 (2)	0.3400 (2)	0.0520 (7)
C8*A*	0.8654 (2)	0.3147 (2)	0.3361 (2)	0.0486 (7)
O9*A*	0.6982 (2)	0.4576 (1)	0.3136 (1)	0.0659 (6)
C9*A*	0.6612 (2)	0.3891 (2)	0.3355 (2)	0.0413 (6)
O10*A*	0.5084 (1)	0.1490 (1)	0.3702 (1)	0.0509 (5)
C10*A*	0.5559 (2)	0.2208 (1)	0.3624 (2)	0.0363 (5)
C11*A*	0.6879 (2)	0.2277 (1)	0.3548 (2)	0.0352 (5)
C12*A*	0.7408 (2)	0.3087 (1)	0.3434 (2)	0.0373 (5)
C13*A*	0.5310 (2)	0.3819 (1)	0.3509 (2)	0.0358 (5)
C14*A*	0.4792 (2)	0.2994 (1)	0.3613 (2)	0.0364 (5)

Table 2. *Selected geometric parameters (Å, °)*

Molecule 1		Molecule 2	
N1—C1	1.476 (3)	N1*A*—C1*A*	1.468 (3)
C1—C13	1.377 (3)	C1*A*—C2*A*	1.378 (3)
C1—C2	1.386 (3)	C1*A*—C13*A*	1.382 (3)
C2—C3	1.359 (3)	C2*A*—C3*A*	1.354 (3)
C3—C4	1.389 (3)	C3*A*—C4*A*	1.387 (3)
O4—C4	1.339 (3)	O4*A*—C4*A*	1.331 (3)
C4—C14	1.417 (3)	C4*A*—C14*A*	1.420 (3)
O5—C5	1.336 (3)	O5*A*—C5*A*	1.338 (3)
C5—C6	1.394 (3)	C5*A*—C6*A*	1.392 (3)
C5—C11	1.402 (3)	C5*A*—C11*A*	1.409 (3)
C6—C7	1.365 (3)	C6*A*—C7*A*	1.364 (3)
C7—C8	1.378 (3)	C7*A*—C8*A*	1.383 (3)
C8—C12	1.382 (3)	C8*A*—C12*A*	1.380 (3)
O9—C9	1.199 (3)	O9*A*—C9*A*	1.210 (2)
C9—C12	1.478 (3)	C9*A*—C12*A*	1.491 (3)

C9—C13	1.483 (3)	C9*A*—C13*A*	1.492 (3)
O10—C10	1.243 (2)	O10*A*—C10*A*	1.243 (2)
C10—C11	1.464 (3)	C10*A*—C11*A*	1.462 (3)
C10—C14	1.467 (3)	C10*A*—C14*A*	1.464 (3)
C11—C12	1.413 (3)	C11*A*—C12*A*	1.408 (3)
C13—C14	1.419 (3)	C13*A*—C14*A*	1.420 (3)
C13—C1—N1	121.9 (2)	C13*A*—C1*A*—N1*A*	122.2 (2)
C2—C1—N1	115.8 (2)	C2*A*—C1*A*—N1*A*	115.7 (2)
O4—C4—C3	117.2 (2)	O4*A*—C4*A*—C3*A*	116.8 (2)
O4—C4—C14	122.9 (2)	O4*A*—C4*A*—C14*A*	123.9 (2)
O5—C5—C6	116.3 (2)	O5*A*—C5*A*—C6*A*	116.8 (2)
O5—C5—C11	124.2 (2)	O5*A*—C5*A*—C11*A*	123.7 (2)
O9—C9—C12	120.6 (2)	O9*A*—C9*A*—C12*A*	121.3 (2)
O9—C9—C13	120.5 (2)	O9*A*—C9*A*—C13*A*	120.8 (2)
O10—C10—C11	120.4 (2)	O10*A*—C10*A*—C11*A*	120.7 (2)
O10—C10—C14	120.1 (2)	O10*A*—C10*A*—C14*A*	119.7 (2)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *DIRDIF* (Beurskens *et al.*, 1994). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, the results of PM3 calculations and a packing diagram have been deposited with the IUCr (Reference: KA1211). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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