Table 3. *Hydrogen-bond and close contact geometry* (Å, °)

DHA	D—H	H···A	D···A	D—H···A
O(5γA)—H···N(1'B')	0.91 (5)	1.82 (5)	2.721 (6)	176 (5)
O(5γB)—H···N(1'A'')	1.03 (7)	1.86 (7)	2.754 (6)	143 (6)
N(4'αA)—H(a)···N(3'B)	1.05 (7)	2.01 (7)	3.059 (7)	178 (3)
N(4'αB)—H(a)···N(3'A)	0.88 (4)	2.19 (4)	3.062 (7)	168 (4)
N(4'αA)—H(b)···O(W)	0.81 (5)	2.33 (5)	3.048 (7)	149 (5)
N(4'αB)—H(b)···N(3B)	0.81 (2)	2.30 (5)	2.928 (7)	135 (5)
O(W)—H(a)···O(5γA''')	1.22 (7)	1.59 (7)	2.798 (7)	171 (5)
O(W)—H(b)···O(5γB'')	0.92 (8)	1.96 (8)	2.896 (6)	159 (8)
N(4'αA)—H(b)···N(3A)	0.81 (2)	2.69 (5)	3.105 (7)	114 (4)

Symmetry code: (none) x, y, z; (i) $x, y, 1 + z$; (ii) $x, y, -1 + z$; (iii) $x, 0.5 - y, -0.5 + z$; (iv) $1 - x, 1 - y, 1 - z$.

overall conformation but there is a small but significant difference in the relative orientations of the two rings, the N(3)—C(35')—C(5')—C(6') torsion angles showing the largest difference of 12.6°. This difference is related to the asymmetric hydrogen-bonding pattern involving the 4'α-amino groups as shown in Fig. 1 and Table 3. Molecule B has a weak

N(4'α)—H···H(3) hydrogen-bonding interaction [H···N(3) 2.30 (5), N···N 2.928 (7) Å, N—H···N 135 (5)°] which has never been observed in any crystal structures of thiamin and its analogues with an intact thiazolium ring. There is no comparable interaction for moleucle A [H···N 2.69 (5) Å]. The packing is shown in Fig. 2.

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Structure of 1,5-Dihydroxyanthraquinone: a Redetermination

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Abstract. $C_{14}H_8O_4$, $M_r = 240.21$, monoclinic, $P2_1/c$, $a = 6.0092 (5)$, $b = 5.3074 (2)$, $c = 15.7538 (6)$ Å, $\beta = 93.672 (5)°$, $V = 501.41 (5)$ Å^3, $Z = 2$, $D_x = 1.591$ g cm^{-3}, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 9.39$ cm^{-1}, $F(000) = 248$, $T = 300$ K, $R = 0.035$, $wR = 0.054$ for 638 reflections [$I \geq 3\sigma(I)$]. The H atom involved in the intramolecular hydrogen bond is found to be asymmetrically placed, with O(1)—H(1) $= 0.94$ Å, and for the intramolecular hydrogen bond O(1)···O(7') $= 2.607 (1)$ Å.

Experimental. The compound was crystallized by the slow diffusion of deionized water into a solution of 1,5-dihydroxyanthraquinone in chromatographically pure acetone at room temperature. An orange parallelpiped crystal of $C_{14}H_8O_4$ having approximate dimensions $0.4 \times 0.4 \times 0.5$ mm was used for data collection on a Rigaku AFC-6R diffractometer using Cu Kα radiation. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 24 carefully centered reflections in the range $40.37 < 2\theta < 49.80°$. The data were collected at a temperature of 300 K using the ω–2θ-scan technique to a maximum 2θ value of 118.10° (h 0→6, k 0→5, l −17→16). ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.280° with a take-off angle of 6.00°. Scans of $(1.26 + 0.30\tan\theta)°$ were made at a speed of 16.00° min^{-1} (in ω).

Of the 880 reflections which were collected, 798 were unique ($R_{int} = 0.015$) and equivalent reflections were merged. The intensities of three representative reflections, measured after every 150 reflections, declined by 0.93% and a linear correction factor was applied. The linear absorption coefficient of Cu Kα is 9.4 cm^{-1}. An empirical absorption correction was also applied (transmission factors 0.95–1.00) and the data were corrected for Lorentz and polarization effects ($p = 0.03$).

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). The non-H atoms were refined with anisotropic thermal parameters. H atoms were located by difference Fourier synthesis and refined with isotropic thermal parameters. Based on 638 observed

reflections [$I > 3\sigma(I)$] and 98 variable parameters, the full-matrix least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ converged with $(\Delta/\sigma)_{max} = 0.11$, and residuals $R = 0.035$, $wR = 0.054$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50×10^{-3} and -0.57×10^{-3} e Å^{-3}, respectively.

Neutral-atom scattering factors and the values for f' and f'' were those of Cromer & Waber (1974). Anomalous-dispersion effects included in F_c were from Ibers & Hamilton (1964). All calculations were performed using the *TEXAN* crystallographic software package (Molecular Structure Corporation, 1985).

An *ORTEPII* (Johnson, 1976) drawing of the title molecule with atom labels is shown in Fig. 1. Fractional coordinates and isotropic thermal parameters of the asymmetric unit are listed in Table 1.* Intramolecular distances and bond angles of the asymmetric unit of 1,5-dihydroxyanthraquinone are listed in Table 2. All heavy atoms lie within 0.02 Å of the plane defined by C(1), C(3) and C(7).

Related literature. The X-ray structure of 1,5-dihydroxyanthraquinone has been determined previously (Hall & Nobbs, 1966) and the agreement factor obtained was quite high ($R = 0.133$). In another refinement an agreement factor of 0.099 was achieved (Guilhelm, 1967a,b). The structures of the parent anthraquinone (Prakash, 1967) and 1,8-dihydroxyanthraquinone (Prakash, 1965) have not been highly refined either, with agreement factors of 0.125 and 0.18, respectively. The quality of data used in the previous determinations is believed to result in such high R values. This work was performed as a part of our continuing study of the excited-state proton-transfer processes of hydroxyanthraquinones (Marasinghe & Gillispie, 1989).

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* Lists of anisotropic thermal parameters of heavy atoms, least-squares-planes data, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55398 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD0070]
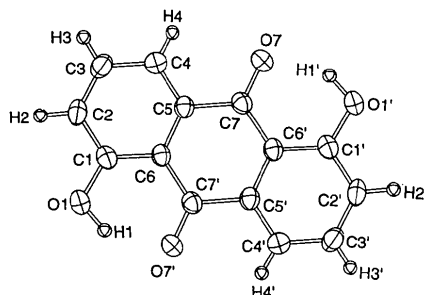

Fig. 1. Drawing of the title molecule with atom labels.

Table 1. *Fractional coordinates and isotropic or equivalent isotropic thermal parameters* (Å^2) *for the 1,5-dihydroxyanthraquinone asymmetric unit*

H atoms were refined isotropically. For anisotropically refined non-H atoms, $B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}]$.

	x	y	z	B_{eq}
O(1)	−0.5037 (2)	−0.1928 (3)	0.11532 (8)	3.58 (7)
O(7)	0.3170 (2)	0.3541 (3)	0.01934 (8)	3.67 (7)
C(1)	−0.3364 (3)	−0.0250 (3)	0.1205 (1)	2.77 (7)
C(2)	−0.3307 (3)	0.1459 (4)	0.1875 (1)	3.20 (8)
C(3)	−0.1656 (3)	0.3226 (4)	0.1970 (1)	3.29 (9)
C(4)	0.0003 (3)	0.3378 (4)	0.1389 (1)	2.94 (8)
C(5)	−0.0033 (3)	0.1709 (3)	0.0722 (1)	2.46 (7)
C(6)	−0.1703 (2)	−0.0143 (3)	0.0615 (1)	2.47 (7)
C(7)	0.1732 (3)	0.1902 (3)	0.0100 (1)	2.57 (7)
H(2)	−0.447 (3)	0.133 (4)	0.226 (1)	3.5 (4)
H(4)	0.108 (3)	0.457 (4)	0.142 (1)	3.0 (4)
H(3)	−0.159 (3)	0.432 (4)	0.240 (1)	3.9 (4)
H(1)	−0.488 (4)	−0.296 (5)	0.068 (2)	5.7 (6)

Table 2. *Intramolecular distances* (Å) *and bond angles* (°) *for the 1,5-dihydroxyanthraquinone asymmetric unit*

O(1)—H(1)	0.94 (3)		C(3)—H(3)	0.88 (2)
O(1)—C(1)	1.341 (2)		C(3)—C(4)	1.397 (2)
O(7)—C(7)	1.229 (2)		C(4)—H(4)	0.90 (2)
C(1)—C(2)	1.389 (3)		C(4)—C(5)	1.373 (2)
C(1)—C(6)	1.408 (2)		C(5)—C(6)	1.408 (2)
C(2)—H(2)	0.96 (2)		C(5)—C(7)	1.493 (2)
C(2)—C(3)	1.367 (3)		C(6)—C(7')	1.462 (2)
H(1)—O(1)—C(1)	109 (1)		H(4)—C(4)—C(3)	123 (1)
O(1)—C(1)—C(2)	117.5 (1)		C(5)—C(4)—C(3)	119.1 (2)
O(1)—C(1)—C(6)	123.1 (2)		C(4)—C(5)—C(6)	121.2 (2)
C(2)—C(1)—C(6)	119.4 (2)		C(4)—C(5)—C(7)	118.8 (2)
H(2)—C(2)—C(3)	122 (1)		C(6)—C(5)—C(7)	120.0 (1)
H(2)—C(2)—C(1)	117 (1)		C(5)—C(6)—C(1)	118.6 (2)
C(3)—C(2)—C(1)	120.8 (2)		C(5)—C(6)—C(7')	120.7 (1)
H(3)—C(3)—C(2)	122 (1)		C(1)—C(6)—C(7')	120.6 (2)
H(3)—C(3)—C(4)	117 (1)		O(7)—C(7)—C(6')	121.2 (1)
C(2)—C(3)—C(4)	120.8 (2)		O(7)—C(7)—C(5)	119.6 (1)
H(4)—C(4)—C(5)	118 (1)		C(6)—C(7')—C(5')	119.2 (2)

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