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1,8-Dinitro-4,5-dihydroxyanthraquinone,* C14H6N2O8

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Abstract. $M_r = 330.21$, monoclinic, $P2_1/a$, $a = 15.664$ (8), $b = 12.056$ (7), $c = 6.704$ (5) Å, $\beta = 94.20$ (5)°, $V = 1262.62$ Å^3, $D_x = 1.737$, $D_m = 1.717$ Mg m^{-3}, $Z = 4$, λ(Cu $K\alpha$) = 1.5418 Å, μ(Cu $K\alpha$) = 1.29 mm^{-1}, $F(000) = 672$, $R = 0.044$ for 1862 observed [$I > 3\sigma(I)$] reflexions. The structure comprises discrete molecules with two internal hydrogen bonds per molecule, and the two nitro groups are inclined by 83.83 (5) and 62.88 (5)° to the anthraquinone nucleus.

Introduction. This work was undertaken as part of a study of the distortions from planarity of a number of substituted anthraquinones which might yield correlations between structure and chemical reactivity. Several of the results of these structure determinations have already been published (Bailey, 1958; Bailey & Brown, 1967*a*,*b c*; Brown & Mitchell, 1982).

Experimental. Sample obtained from Imperial Chemical Industries Limited (Organics Division), acicular crystals suitable for X-ray diffraction measurements grown from phenol solution, strongly pleochroic, showing purple and brown shading; unit-cell dimensions obtained initially from rotation photographs, and more accurately from high-angle reflexions on Weissenberg photographs by a least-squares analysis of the $\alpha_1\alpha_2$ separations; crystal 2.0 × 0.2 × 0.2 mm for collecting intensity data; Nonius integrating Weissenberg camera at University College London; multiple-film photographs taken about **b** (zero level) and **c** (zero and five levels), intensities derived from a combination of visual and optical measurements using a Joyce–Loebl microdensitometer; 2316 measured reflexions; structure solved by a combination of a sharpened three-dimensional Patterson synthesis and manually derived $\sum_2$ relationships; signs of 171 independent structure amplitudes thereby obtained, the resulting E map showing all the non-hydrogen atoms; parameters refined by least-squares calculations using B_{ij} and $w = 1/F$ until shifts were all less than 0.5σ; positional parameters for the six H atoms obtained from a difference Fourier map, and these, together with their B_{iso}, were refined until the shifts were less than σ; $R_w = 0.058$; scattering factors from *International Tables for X-ray Crystallography* (1962); computer programs used included some local compilations on the IBM 360/65 at University College London, but were mainly those of the NRC series (Ahmed, Hall, Pippy & Huber, 1970) implemented on the ICL 1905E at the London Polytechnics Computer Unit.

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* IUPAC nomenclature: 1,8-dihydroxy-4,5-dinitroan-thraquinone.

Table 1. *Final atomic parameters and e.s.d.'s*

$$B_{eq} = \tfrac{1}{3}(B_{11} + B_{22} + B_{33}).$$

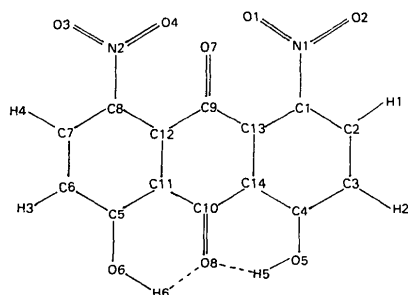|	x	y	z	$B_{eq}(\text{Å}^2)$
C(1)	0·0218 (2)	0·2127 (2)	0·3913 (4)	3·23 (3)
C(2)	−0·0375 (2)	0·1984 (2)	0·5335 (5)	3·84 (3)
C(3)	−0·0430 (2)	0·2756 (2)	0·6822 (5)	4·04 (3)
C(4)	0·0125 (2)	0·3657 (2)	0·6937 (4)	3·76 (3)
C(5)	0·2450 (1)	0·5852 (2)	0·4182 (4)	3·21 (3)
C(6)	0·3037 (2)	0·5997 (2)	0·2758 (5)	3·74 (3)
C(7)	0·3128 (2)	0·5205 (2)	0·1317 (4)	3·73 (3)
C(8)	0·2616 (2)	0·4267 (2)	0·1281 (4)	3·25 (3)
C(9)	0·1369 (1)	0·3190 (2)	0·2373 (4)	2·86 (2)
C(10)	0·1291 (2)	0·4776 (2)	0·5609 (4)	3·44 (3)
C(11)	0·1920 (1)	0·4917 (2)	0·4121 (4)	3·03 (3)
C(12)	0·1995 (1)	0·4120 (2)	0·2617 (4)	2·84 (3)
C(13)	0·0761 (1)	0·3033 (2)	0·3957 (4)	2·99 (3)
C(14)	0·0724 (2)	0·3814 (2)	0·5488 (4)	3·23 (3)
N(1)	0·0246 (1)	0·1246 (2)	0·2399 (4)	3·69 (3)
N(2)	0·2807 (1)	0·3407 (2)	−0·0178 (4)	3·53 (3)
O(1)	0·0782 (2)	0·0507 (2)	0·2785 (4)	5·74 (3)
O(2)	−0·0259 (2)	0·1292 (2)	0·0960 (4)	5·94 (4)
O(3)	0·3075 (1)	0·2512 (2)	0·0484 (3)	4·35 (3)
O(4)	0·2751 (1)	0·3659 (2)	−0·1932 (3)	4·41 (3)
O(5)	0·0026 (1)	0·4379 (2)	0·8419 (3)	4·46 (3)
O(6)	0·2428 (1)	0·6652 (2)	0·5586 (3)	4·19 (2)
O(7)	0·1301 (1)	0·2645 (2)	0·0839 (3)	3·89 (2)
O(8)	0·1242 (1)	0·5467 (2)	0·6969 (3)	3·85 (2)
H(1)	−0·089 (3)	0·131 (3)	0·493 (7)	5·40 (83)
H(2)	−0·088 (3)	0·263 (4)	0·786 (7)	3·53 (61)
H(3)	0·341 (3)	0·667 (4)	0·274 (7)	3·84 (60)
H(4)	0·341 (3)	0·530 (4)	0·005 (7)	2·58 (51)
H(5)	0·044 (3)	0·491 (4)	0·860 (6)	6·23 (84)
H(6)	0·181 (3)	0·647 (3)	0·624 (7)	5·38 (90)

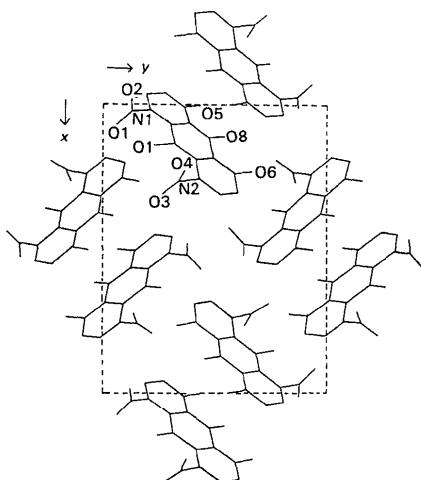Fig. 1. Diagram of molecule showing numbering of atoms (hydrogen bonds dashed).

Fig. 2. Projection of structure on (001) (H atoms omitted).

Discussion. The final positional and equivalent isotropic temperature parameters are given in Table 1.* The numbering of the atoms is shown in Fig. 1. The crystal structure consists of separate molecules (Fig. 2) held together by van der Waals forces. The possibility of a stronger intermolecular interaction between O(5) atoms across centres of symmetry evinced by the short O(5)···O(5') distance [2·601 (3)] Å is not supported by the position of H(5) on the difference map. Bond lengths and interbond angles and their e.s.d.'s are given in Table 2. These agree well with those found in comparable structures; mean values of groups of bonds are compared with the values found in the isomeric 1,5-dinitro-4,8-dihydroxyanthraquinone (Bailey & Brown, 1967a) shown in brackets: mean C—C in benzene ring 1·389 (1·383), mean C—C in central ring 1·476 (1·467), mean C=O 1·229 (1·219), mean C—OH 1·347 (1·336), mean N=O 1·220 (1·183), mean C—N 1·469 (1·477) Å. With e.s.d.'s ±0·004 Å in this structure, and ± 0·005 Å in the 1,5-dihydroxy isomer, the mean bond lengths in the two structures are reasonably compatible with the exception of the N—O lengths in the nitro group. Pauling's (1944) prediction

Table 2. *Bond distances (Å) and angles (°)*

C(1)—C(13)	1·383 (3)	C(9)—C(13)	1·490 (3)
C(1)—C(2)	1·390 (4)	C(10)—C(11)	1·462 (4)
C(2)—C(3)	1·372 (4)	C(10)—C(14)	1·460 (4)
C(3)—C(4)	1·389 (4)	C(1)—N(1)	1·472 (4)
C(4)—C(14)	1·412 (4)	C(8)—N(2)	1·471 (4)
C(13)—C(14)	1·397 (4)	C(4)—O(5)	1·339 (4)
C(5)—C(11)	1·399 (3)	C(5)—O(6)	1·349 (3)
C(5)—C(6)	1·384 (4)	C(9)—O(7)	1·218 (3)
C(6)—C(7)	1·373 (4)	C(10)—O(8)	1·242 (3)
C(7)—C(8)	1·386 (4)	N(1)—O(1)	1·238 (3)
C(8)—C(12)	1·382 (3)	N(1)—O(2)	1·203 (4)
C(11)—C(12)	1·404 (4)	N(2)—O(3)	1·228 (3)
C(9)—C(12)	1·490 (4)	N(2)—O(4)	1·212 (3)
C(13)—C(1)—C(2)	121·6 (2)	C(11)—C(10)—O(8)	120·3 (2)
C(13)—C(1)—N(1)	122·3 (2)	C(14)—C(10)—O(8)	120·2 (2)
C(2)—C(1)—N(1)	116·0 (2)	C(5)—C(11)—C(10)	120·1 (2)
C(1)—C(2)—C(3)	119·6 (3)	C(5)—C(11)—C(12)	119·5 (2)
C(2)—C(3)—C(4)	120·0 (3)	C(10)—C(11)—C(12)	120·4 (2)
C(3)—C(4)—C(14)	120·7 (3)	C(8)—C(12)—C(9)	121·0 (2)
C(3)—C(4)—O(5)	116·3 (2)	C(8)—C(12)—C(11)	118·5 (2)
C(14)—C(4)—O(5)	122·8 (2)	C(9)—C(12)—C(11)	120·3 (2)
C(11)—C(5)—C(6)	120·2 (2)	C(1)—C(13)—C(9)	120·6 (2)
C(11)—C(5)—O(6)	123·4 (2)	C(1)—C(13)—C(14)	119·3 (2)
C(6)—C(5)—O(6)	116·3 (2)	C(9)—C(13)—C(14)	120·0 (2)
C(5)—C(6)—C(7)	120·4 (3)	C(4)—C(14)—C(10)	120·1 (2)
C(6)—C(7)—C(8)	119·3 (3)	C(4)—C(14)—C(13)	118·7 (2)
C(7)—C(8)—C(12)	121·9 (2)	C(10)—C(14)—C(13)	121·2 (2)
C(7)—C(8)—N(2)	116·2 (2)	C(1)—N(1)—O(1)	115·4 (2)
C(12)—C(8)—N(2)	121·8 (2)	C(1)—N(1)—O(2)	117·9 (2)
C(12)—C(9)—C(13)	117·9 (2)	O(1)—N(1)—O(2)	126·6 (3)
C(12)—C(9)—O(7)	120·9 (2)	C(8)—N(2)—O(3)	117·3 (2)
C(13)—C(9)—O(7)	120·8 (2)	C(8)—N(2)—O(4)	117·7 (2)
C(11)—C(10)—C(14)	119·5 (2)	O(3)—N(2)—O(4)	124·7 (2)

for this was 1·19 Å, but experimentally determined values have a wide spread from 1·14 to 1·27 Å. The recent accurate determination of p-dinitrobenzene (Di Rienzo, Domenicano & Riva di Sanseverino, 1980) gave 1·218 and 1·220 (2) Å for N=O, and the electron diffraction analysis of the same structure gave 1·219 (2) Å (Sadova, Popik, Vilkov, Pankrushev & Shlyapochnikov, 1974), which agree well with our mean value of 1·220 (3) Å. It is noteworthy that in our structure one of the N—O bonds in each nitro group is longer than the other (mean values 1·233 and 1·208 Å).

In the case of the C=O bonds, that where the O accepts two hydrogen bonds is longer than the other (1·242 compared with 1·218 Å). Evidence for H(5) bonding to O(8) rather than to O(5′) is that the distance H(5)···O(8) is 1·857 (44) compared with H(5)···O(5′)=2·334 (43) Å. The direct distances O(5)···O(8) and O(6)···O(8) are 2·562 (3) and 2·569 (3) Å respectively, whereas the distances via the H atoms, O(5)—H(5)···O(8) and O(6)—H(6)···O(8), are 2·767 and 2·709 Å, involving angles at H(5) of 132·6 (3·5) and at H(6) of 142·4 (3·7)°.

The mean atomic deviation from the plane of the anthraquinone nucleus [atoms C(1)—C(14)] is

0·028 (2) Å. The mean deviation from the plane of nitro group C(1), N(1), O(1), O(2) is 0·005 (2) Å and from nitro group C(8), N(2), O(3), O(4) is 0·014 (2) Å. The dihedral angles between the anthraquinone nucleus and the two nitro groups are 83·83 (5) and 62·88 (5)° respectively, and the angle between the two nitro groups is 144·12 (5)°.

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2,5-Bis(1,1,3,3-tetramethylbutyl)-1,4-benzoquinone, C22H36O2

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Abstract. $M_r = 332 \cdot 52$, monoclinic, $P2_1/a$, $a = 11 \cdot 912$ (12), $b = 15 \cdot 586$ (12), $c = 6 \cdot 542$ (10) Å, $\beta = 119 \cdot 37$ (10)°, $V = 1058 \cdot 48$ Å^3, $D_x = 1 \cdot 043$, $D_m = 1 \cdot 035$ Mg m^{-3}, $Z = 2$, $\lambda(\text{Cu}\,K\alpha) = 1 \cdot 5418$ Å, $\mu(\text{Cu}\,K\alpha) = 0 \cdot 50$ mm^{-1}, $F(000) = 368$, $R = 0 \cdot 060$ for 723 observed $[I > 3\sigma(I)]$ reflexions. The structure comprises discrete centrosymmetrical molecules with no strong intermolecular forces.

Introduction. The material supplied by Kodak Limited was known to be diisooctylbenzoquinone, and one reason for undertaking this work was to determine which of the 80 or more octyl isomers was present. Another reason was the relative scarcity of accurate structural data on quinones.

Experimental. Golden-yellow acicular crystals (m.p. 411 K) from aqueous ethanol solution, elemental

analysis gave C 79·50, H 10·80% (required for C22H36O2, C 79·50, H 10·80%); unit-cell dimensions obtained initially from rotation photographs and more accurately from 2θ measurements on Weissenberg photographs, intensity data obtained by the multiple-film technique and visual comparison of densities with a calibrated scale on photographs about **c** (0–5 levels), inter-layer scaling and cross-correlation made using a zero-level **b** Weissenberg photograph; 1166 measured reflexions; data reduction and structure determination carried out using the NRC suite of programs (Ahmed, 1970) on the ICL 1905E computer at the London Polytechnics Computer Unit; the E map obtained from 135 reflexions with $E \geq 1 \cdot 5$ showed all the non-H atoms; positional parameters, together with isotropic temperature factors, starting from the Wilson-plot value ($B = 2 \cdot 86$ Å^2), refined by least squares to $R = 0 \cdot 10$; weights $w = 1/F_o$; H atoms, obtained by a combination